

# THE $\pi$ -ELECTRON DISTRIBUTION IN PYRIDINE AND THE MOLECULAR-ORBITAL PARAMETERS FOR NITROGEN

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## Summary

The  $\pi$ -electron distribution in pyridine has been calculated by the self-consistent-field molecular-orbital method, including electron interaction explicitly. Empirical parameters analogous to the coulomb parameters in the simple molecular-orbital theory are not required in the calculations.

The results have been compared with chemical properties of pyridine and have also been used to determine the most suitable values for the coulomb parameters in the simple molecular-orbital treatment of pyridine. It emerges that, in addition to a coulomb parameter to allow for the electronegativity of nitrogen being greater than that of carbon, an appreciable auxiliary coulomb parameter, representing an enhanced electronegativity of carbon atoms adjacent to the hetero-atom, must be introduced. This auxiliary parameter is necessary to allow for purely  $\pi$ -electron effects in the vicinity of a hetero-atom and is additional to any parameter which might be required owing to  $\sigma$ -electron polarization effects around the nitrogen atom.

## I. INTRODUCTION

The simple molecular-orbital treatment of conjugated systems has proved to be a satisfactory basis for predicting and correlating chemical properties of conjugated hydrocarbon systems (Brown 1952; Dewar, Mole, and Warford 1956). However, the extension of this theoretical treatment to conjugated heterocyclic systems has been handicapped by the "problem of hetero-parameters", numerical parameters must be introduced to allow for the fact that hetero-atoms do not have the same electronegativities as carbon atoms, and the magnitude and, in certain circumstances, the sign of these parameters has been a matter for controversy. Thus the coulomb parameter,  $h$ , for nitrogen in molecules such as pyridine, has been assigned values from +2 to +0.5 (cf. Brown 1956) and although it now seems certain that a tertiary nitrogen carrying a large negative charge, such as exists in the imidazolate anion, has a negative value of  $h$ , the magnitude is at present unknown (Bassett, Brown, and Penfold 1956).

In order to improve our knowledge of the appropriate values of  $h$  for nitrogen atoms in various environments we therefore sought to estimate this parameter directly from theoretical principles. The more elaborate self-consistent-field molecular-orbital treatment (Roothaan 1951) can provide values for the distribution of  $\pi$ -electrons in heterocycles without empirically requiring the value of any parameter analogous to  $h$ ; the coulomb integrals in this theory may instead be

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evaluated directly from the molecular hamiltonian.\* Having obtained the charge distribution in a heterocycle by the SCF procedure it is easy to determine the value of  $h$  required in the simple theory to reproduce the SCF results.

This approach has already been used to study nitrogen atoms in the simple systems  $\text{CH}_2=\text{NH}$ ,  $\text{CH}_2=\text{NH}_2^+$ , and  $\text{CH}_2=\text{N}^-$  (Brown and Penfold 1957) and we have now extended our study to pyridine in order to study the "auxiliary inductive parameter". This is a second parameter,  $h'$ , introduced to allow for the assumption that carbon atoms adjacent to nitrogen atoms (or other hetero-atoms) are rendered more electronegative than unperturbed carbon atoms owing to an inductive effect. The soundness of this assumption, that is, that  $h'$  must be assigned a value appreciably different from zero, does not appear to have been established hitherto.

## II. METHOD

Full details of the methods used to evaluate the various integrals arising in the SCF molecular-orbital method have been given by Brown and Penfold (1957) and so will not be repeated here.

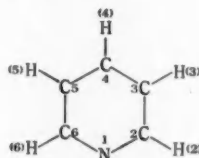


Fig. 1

The geometry of pyridine has now been established with some precision (Bak 1955); the various internuclear distances occurring in the molecular integrals are set out in Table 1, the numbering being that of Figure 1. The

TABLE 1  
INTERNUCLEAR DISTANCES IN PYRIDINE

Atoms	Distance (Å)	Atoms	Distance (Å)	Atoms	Distance (Å)
$\text{N}_1\text{C}_2$	1.340	$\text{C}_3\text{C}_5$	2.674	$\text{N}_1\text{H}_2$	2.058
$\text{C}_2\text{C}_3$	1.390	$\text{C}_3\text{C}_5$	2.402	$\text{C}_2\text{H}_3$	2.147
$\text{C}_3\text{C}_4$	1.400	$\text{C}_4\text{C}_5$	2.386	$\text{C}_3\text{H}_2$	2.151
$\text{N}_1\text{C}_6$	2.411	$\text{C}_2\text{H}_2$	1.085	$\text{C}_2\text{H}_4$	2.160
$\text{N}_1\text{C}_4$	2.813	$\text{C}_3\text{H}_3$	1.080	$\text{C}_4\text{H}_3$	2.165
$\text{C}_2\text{C}_6$	2.228	$\text{C}_4\text{H}_4$	1.075		

\* Since we follow Parr and Pariser (1953) in using the "atoms in molecules" treatment (Moffitt 1951), the coulomb integrals for carbon and nitrogen are based on energies of various spectroscopic states of the isolated atoms and their positive and negative ions. It is of course more convenient to use experimental spectroscopic data for these states than to compute the relevant energies to the required accuracy by very elaborate theoretical treatments of these mononuclear systems.

values of the basic molecular integrals arising in our calculations are given in Tables 2, 3, and 4. It may be noted that the hydrogen penetrations, of which all those having appreciable values are given in Table 4, have almost universally been ignored by previous investigators, although an attempt has been made to

TABLE 2  
COULOMB REPULSION INTEGRALS

Integral	Value (eV)	Integral	Value (eV)
(11   11)	12.82	(22   66)	5.79
(11   22)	7.90	(33   33)	11.08
(11   33)	5.56	(33   44)	7.45
(11   44)	4.89	(33   55)	5.50
(22   22)	11.08	(44   44)	11.08
(22   33)	7.47	(55   55)	11.08
(22   44)	5.51	(66   66)	11.08
(22   55)	5.06		

TABLE 3  
COULOMB PENETRATION INTEGRALS FOR RING ATOMS

Integral	Value (eV)	Integral	Value (eV)
(2 : 11)	0.921	(2 : 55)	0.004
(3 : 11)	0.009	(2 : 66)	0.028
(4 : 11)	0.002	(1 : 33)	0.447
(1 : 22)	1.655	(3 : 44)	0.758
(2 : 33)	0.787	(3 : 55)	0.013
(2 : 44)	0.015	(1 : 44)	0.349

TABLE 4  
HYDROGEN PENETRATION INTEGRALS

Integral	Value (eV)	Integral	Value (eV)
(H <sub>2</sub> : 11)	0.021	(H <sub>3</sub> : 33)	0.597
(H <sub>2</sub> : 22)	0.598	(H <sub>3</sub> : 44)	0.017
(H <sub>2</sub> : 33)	0.018	(H <sub>4</sub> : 33)	0.018
(H <sub>3</sub> : 22)	0.018	(H <sub>4</sub> : 44)	0.597

justify this approximation (Jørgensen and Pullman 1955). The hydrogen penetrations are particularly important in the treatment of conjugated systems which include nitrogen atoms and if these integrals are ignored the resultant  $\pi$ -electron densities are appreciably changed. For the SCF calculations, a set of molecular orbitals is required to commence the iterative process. For convenience we used the

orbitals obtained by the simple molecular-orbital treatment for a coulomb parameter  $h = +0.5$  since we believed these orbitals to lie near the SCF orbitals. The difference between the two sets was greater than we anticipated; the  $\pi$ -electron densities corresponding to our initial set of molecular orbitals and the final SCF charge distribution are listed in Table 5.

TABLE 5  
CHARGE DISTRIBUTION IN PYRIDINE

	Simple Molecular Orbital $h = 0.5$	Self-Consistent Field Molecular Orbital
$q_1$	1.296	1.061
$q_2$	0.923	0.999
$q_3$	1.004	0.983
$q_4$	0.950	0.974

### III. COMPARISON OF CHEMICAL PROPERTIES WITH THE SCF CHARGE DISTRIBUTION

It is well known (e.g. Brown 1952) that the charge distribution in a conjugated system need not necessarily correlate directly with the chemical reactivities of the various positions because the chemical "non-crossing rule" may break down. Nevertheless, in the absence of localization energy data, it is interesting to see to what extent such direct correlation happens to exist. (The chemistry of pyridine has been discussed in some detail in the light of simple molecular-orbital calculations by Brown and Heffernan (1956) and may be summarized as follows. Electrophilic substitution is complicated by protonation of pyridine but the attack occurs preferentially at the 3-position. Nucleophilic substitution favours the 2- and 4-positions but there is almost no cleant evidence of the relative reactivities of these positions.) The amination and arylation reactions, cited in our previous paper, are of uncertain mechanism, and the observed hydroxylation of pyridine in the 2-position cannot be accepted without reservation because the yield of product was not recorded. The reactions of picolines with aldehydes clearly indicate a greater reactivity for a 2-methyl group than for a 4-methyl, but these reactions were performed in the presence of acid, or of electrophils such as  $ZnCl_2$ , so that it is presumably the reactivities of the corresponding pyridinium systems which are demonstrated in this work. However, we have recently noticed two further pieces of evidence relating to the uncharged pyridine system. Chapman and Russell-Hill (1954) found that the halogen in 4-chloropyridine is more readily displaced by nucleophils than is the halogen in 2-chloropyridine. Furthermore, the order of basicities of the aminopyridines is  $4 < 2 < 3$  (Albert, Goldacre, and Phillips 1948).

The charge distribution obtained by the SCF method corresponds to an increase in the  $\pi$ -electron density in the order  $4 < 3 < 2^*$  and this does not fully

\* A  $\pi$ -electron distribution in very close agreement with the SCF result has now been obtained by an ASMOCI treatment of pyridine (Brown and Heffernan, in press).



reflect the chemistry in that the charge at the 3-position would be expected to be greater than that at the 2-position. However, it is likely that the localization energies for electrophilic and nucleophilic substitutions will fall in sequences such that the discrepancy between  $\pi$ -electron densities and chemistry may be attributed to a breakdown of the chemical "non-crossing rule" (Brown 1952). Certainly the localization energies obtained by the simple MO method show a strong localization preference for the 3-position in electrophilic substitution and for the 2- and 4-positions in nucleophilic attack.

It is interesting that a calculation of the charge distribution by a simple SCF molecular-orbital method, not including electron interaction explicitly, gives a charge distribution in the order  $3 < 4 < 2$  (Pritchard and Sumner 1956) which is grossly at variance with chemical properties.

#### IV. VALUES OF COULOMB PARAMETERS IN THE SIMPLE MO CALCULATIONS

It is easy to determine what values must be assigned to coulomb integrals in the simple molecular-orbital method to yield the same values for  $\pi$ -electron densities as were obtained in the SCF calculation. The latter are all close to unity and so the mutual atom polarizabilities  $\pi_{\mu,\nu}^0$  for benzene may be used.\* Since only three independent coulomb parameters occur we may for convenience take  $h_4=0$  and then we obtain the following linear equations:

$$\begin{aligned} q_1^0 &= 1 + \lambda_{1,1}h_1 + 2\lambda_{1,2}h_2 + 2\lambda_{1,3}h_3, \\ q_2^0 &= 1 + \lambda_{1,2}h_1 + (\lambda_{1,1} + \lambda_{1,3})h_2 + (\lambda_{1,2} + \lambda_{1,4})h_3, \\ q_3^0 &= 1 + \lambda_{1,3}h_1 + (\lambda_{1,2} + \lambda_{1,4})h_2 + (\lambda_{1,1} + \lambda_{1,3})h_3, \end{aligned}$$

where  $\lambda_{\mu,\nu}$  is the polarizability magnitude, that is,

$$\lambda_{\mu,\nu} = \partial q_{\mu}^0 / \partial h_{\nu}.$$

Upon substituting the SCF values for  $q_1^0$ ,  $q_2^0$ , and  $q_3^0$  and the numerical values for the polarizability magnitudes of benzene (Coulson and Longuet-Higgins 1947) and solving the linear equations we find:

$$h_1 = 0.227, \quad h_2 = 0.093, \quad h_3 = 0.013.$$

However, it is possible to derive a charge distribution very similar to the SCF distribution by using only two coulomb parameters, that is, taking  $h_3 = h_4 = 0$ .

\* The use of the polarizabilities for benzene is equivalent to determining what small perturbations to benzene will produce the charge distribution of pyridine. The question of the appropriate value to use for the C:N resonance integral is unimportant because for benzene (and other alternant hydrocarbons, see Coulson and Longuet-Higgins 1947)  $\partial q_{\mu}^0 / \partial \beta_{\mu\lambda}^0 = 0$ , that is, for small perturbations the charge distribution is independent of resonance integrals. Thus the present considerations of coulomb parameters in the simple molecular-orbital theory tacitly assume that  $\beta_{\text{CN}}^0$  is not vastly different from  $\beta_{\text{CC}}^0$ . Some independent evidence already exists (Brown 1956) that these resonance integrals in the simple molecular-orbital theory are similar. For the SCF calculations,  $\beta_{\text{CN}}$  was evaluated from spectroscopic data to be  $-2.47$  eV,  $\beta_{\text{CC}}$  (for a rather greater internuclear distance) being  $-2.39$  eV (Brown and Penfold 1957; Brown, Heffernan, and Penfold, unpublished data).

With  $h_1=0.220$  and  $h_2=0.083$ , these values being selected to reproduce exactly the SCF values for  $q_1^0$  and  $q_2^0$ , the  $\pi$ -electron densities are found to be:

$$q_1^0=1.061, \quad q_2^0=0.999, \quad q_3^0=0.981, \quad q_4^0=0.979.$$

These values are very similar to the SCF values for all four positions, the main deviation being that  $q_3^0$  and  $q_4^0$  do not differ as much as do the SCF values for the 3- and 4-positions. An alternative set of two parameters which reproduces the SCF values closely for the carbon atoms at the cost of a rather larger deviation for the  $\pi$ -electron density on the nitrogen atom is  $h=0.25$ ,  $h'=0.08$ . The resultant charge distribution is

$$q_1^0=1.074, \quad q_2^0=0.993, \quad q_3^0=0.982, \quad q_4^0=0.976.$$

It is not possible to obtain a charge distribution with only one coulomb parameter in the simple MO theory which closely resembles the SCF distribution.

These results have considerable bearing on the controversial question of auxiliary inductive parameters. In the simple MO calculations, Wheland and Pauling (1935) first introduced small coulomb parameters for carbon atoms adjacent to nitrogen to allow for the polarization of C-N  $\sigma$ -electrons in the sense  $C^+-N^-$ . The small positive charge thus induced on the carbon would enhance its electronegativity. The controversial point is the magnitude of this effect. Pauling and Wheland used an auxiliary inductive parameter equal to 1/10th of the main hetero-parameter because the  $\pi$ -electron densities obtained using these parameters appeared to be in best agreement with the chemical properties of the molecules. However, the theoretical interpretation of chemical properties is now known to be more complex (e.g. Brown 1952) and so Wheland and Pauling's (1935) argument loses its force. A second line of argument was used by Dewar (1949), who prescribed inductive coulomb parameters falling off in geometrical progression based on properties of aliphatic carboxylic acids; this proposed inductive effect was much larger than that proposed by Wheland and Pauling, the parameters being  $h_n=(1/3)^n$ .\* However, in spite of considerable theoretical work on conjugated heterocyclic systems no discrepancy between theory and experiment, definitely ascribable to omission of auxiliary inductive parameters rather than to other defects of the molecular-orbital method, has yet been revealed.

The significant aspect of the present SCF results is that in spite of the fact that they were obtained assuming *no* polarization of  $\sigma$ -electrons for evaluation of the core hamiltonian, an appreciable auxiliary inductive parameter is required ( $h' \approx h/3$ ) to reproduce the same results in the simple theory. Thus purely  $\pi$ -electronic interactions call for an auxiliary inductive effect. An additional auxiliary parameter may yet be required to allow for  $\sigma$ -electron polarization, but this must await a more detailed theoretical treatment of the core of conjugated systems.

\* We have tried to reproduce the SCF results using the simple molecular-orbital theory with coulomb parameters of the form  $h_n=y(\sigma)^n$ , but such parameters were found incapable of producing  $\pi$ -electron densities resembling the SCF values.

## V. ACKNOWLEDGMENT

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# THE MOLAR KERR CONSTANTS, DIPOLE MOMENTS, AND RELAXATION TIMES OF METHYL AND ETHYL MALEATES AND FUMARATES, ETHYL FORMATE, DIETHYL OXALATE, AND OF ETHYL AND PROPYL AZODIFORMATES

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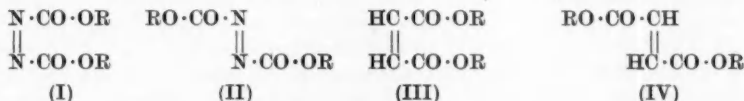
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## Summary

Values for the properties and compounds named in the title are recorded at infinite dilution in carbon tetrachloride at 25 °C. Dipole moments of the seven diesters lie between 2.2 and 2.8 D; the molar Kerr constants of the two azodiformates however differ from those of the maleates, fumarates, and oxalate in being negative. Results with ethyl oxalate are consistent with a structure in which the two  $-\text{CO}_2\text{Et}$  groups are in planes making an azimuthal angle c. 90°. Indications of configurations for the other esters are discussed, but conclusions are indefinite.

## I. INTRODUCTION

Alkyl azodiformates ( $\text{RO}\cdot\text{CO}\cdot\text{N}=\text{N}\cdot\text{CO}\cdot\text{OR}$ ) have been known since the work of Curtius and Heidenreich (1894). As with many other  $-\text{N}=\text{N}-$  containing molecules, they appear to occur in one form only (cf. references quoted by Le Fèvre and Sousa 1955), but no evidence is extant on whether the single configuration is *cis*-I or *trans*-II. Thus the present measurements were



made in the hope that comparisons with alkyl maleates (III) and alkyl fumarates (IV) would assist a decision on the point. The properties studied have been the dipole moments, the dielectric relaxation times, and the molar Kerr constants.

## II. EXPERIMENTAL

The fumaric and maleic esters were prepared by direct esterification of the acids; for the two azodiformates Vogel's (1952) directions (see Cresswell *et al.* 1952) were followed; b.p.'s or m.p.'s in agreement with values given in the literature for pure specimens were achieved without difficulty.

The three properties mentioned above have all been determined with carbon tetrachloride as a solvent. Details of apparatus, procedures, etc. may be found as follows: dielectric constants, Buckingham *et al.* (1956); general

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experimental technique, and methods of dipole moment calculation, Le Fèvre (1953); relaxation times, Le Fèvre and Sullivan (1954); molar Kerr constants, Le Fèvre and Le Fèvre (1953, 1955). For convenience, symbols used are listed here, subscripts 1, 2, and 12 indicating, where appropriate, solvent, solute, and solution respectively:

$w_2$  = weight fraction of solute in a solution,

$\epsilon$  = dielectric constant,

$d$  = density,

${}_T P$  = total molecular polarization,

${}_D P$  = distortion polarization,

$R$  = molecular refraction,

$\mu$  = dipole moment,

$\alpha\epsilon_1 = [(\epsilon_{12} - \epsilon_1)/w_2]_{w_2=0}$ ,

$\beta d_1 = [(d_{12} - d_1)/w_2]_{w_2=0}$ ,

$n$  = refractive index,

$\gamma n_1 = \Sigma(n_{12} - n_1)/\Sigma w_2$ ,

$\Delta f$  = width of resonance curve at half-height, in Mc/s,

$Q$  = "Q" factor of circuit,

$\Delta \tan \delta'$  = change of loss tangent from solvent to solution,

$\psi = (\Delta \tan \delta')/w_2$ ,

$\tau$  = relaxation time of solute,

$B$  = Kerr constant,

$\Delta B = B_{12} - B_1$ ,

$B_1 \delta = B \Delta / w_2$ ,

$b_i, b_j, b_k$  = semi-axes of a polarizability ellipsoid,

${}_s K_1$  = specific Kerr constant of solvent,

${}_m K_2$  = molar Kerr constant of solute.

Observations are presented in Tables 1-3 and results in Table 4. Regarding the latter, it should be noted that the following methods of calculation have been adopted:

$$(\alpha\epsilon_1)_{w_2=0} = \Sigma(\epsilon_{12} - \epsilon_1)/\Sigma w_2,$$

$$(\beta)_{w_2=0} = \Sigma(d_{12} - d_1)/d_1 \Sigma w_2,$$

$$(\psi)_{\text{mean}} = \Sigma(\Delta \tan \delta')/\Sigma w_2,$$

$$(\delta)_{w_2=0} = a/B_1,$$

where  $a$  is obtained from the equation

$$10^7 \Delta B = a w_2 + b w_2^2.$$

In the single instance of ethyl formate the quantities  $\Delta\epsilon = \epsilon_{12} - \epsilon_1$  and  $\Delta d = d_{12} - d_1$  have also been fitted to regression equations of the type  $\Delta\epsilon$ , or  $\Delta d$ ,  $= a w_2 + b w_2^2$ , whence  $(\alpha\epsilon_1)_{w_2=0}$  or  $(\beta d_1)_{w_2=0}$  follow as the  $a$  terms in each case. This procedure was rendered desirable because the  $\epsilon_{12}$  and  $d_{12}$  values observed showed curvature when plotted against  $w_2$  (cf. Harris, Le Fèvre, and Sullivan 1953).

## III. DISCUSSION

The polarities now found for ethyl formate (2.0<sub>1</sub> D) and for diethyl oxalate (2.4<sub>1</sub> D) are in reasonable accord with earlier values (see Zahn 1932; Wesson 1948). No previous mention of the dipole moments of dimethyl maleate or fumarate can be found in the literature. For the two ethyl esters, Smyth and

TABLE I  
DIELECTRIC POLARIZATION MEASUREMENTS IN CARBON TETRACHLORIDE AT 25 OR 30 °C

Compound	$10^6 w_2$	$\epsilon_{12}$	$d_{12}$	$10^6 w_2$	$\epsilon_{12}$	$d_{12}$
Dimethyl fumarate at 25 °C	0	2.2270	1.58454	12121	2.3076	1.57651
	7684	2.2782	1.57929	17508	2.3431	1.57323
	7782	2.2786	1.57926	18695	2.3517	1.57258
Dimethyl maleate at 25 °C	4272	2.2617	1.58124	10205	2.3108	1.57823
	4870	2.2662	1.58126	13337	2.3269	1.57645
	6579	2.2830	1.57952	15101	2.3504	1.57475
Diethyl fumarate at 25 °C	4725	2.2574	1.57988	12190	2.3037	1.57486
	7077	2.2714	1.57830	19908	2.3524	1.56839
	10876	2.2956	1.57484	21026	2.3586	1.56686
Diethyl maleate at 25 °C	6909	2.2785	1.57988	19929	2.3766	1.56944
	9966	2.3011	1.57643	31783	2.4603	1.56045
	18072	2.3602	1.57056			
Diethyl azodiformate at 25 °C	5030	2.2634	1.58184	20603	2.3775	1.57000
	10858	2.3064	1.57753	21292	2.3778	1.56981
	14290	2.3306	1.57429	21889	2.3821	1.56946
Di- <i>n</i> -propyl azodiformate at 25 °C	2492	2.2432	1.58247	26847	2.4219	1.56442
	5695	2.2673	1.58066	29337	2.4396	1.56253
	11348	2.3088	1.57628			
Ethyl formate at 30 °C	0	2.2176	1.57480	4352	2.2571	1.56944
	1035	2.2293	1.57321	4799	2.2611	1.56874
	1067	2.2293	1.57323	6027	2.2730	1.56737
	1959	2.2361	1.57209	7766	2.2882	1.56533
whence $\Delta\epsilon = 1.58_3 w_2 - 70.4 w_2^2$ $\Delta d = -1.362 w_2 + 19.8 w_2^2$						
Diethyl oxalate at 25 °C	1162	2.2356	—	5859	2.2706	1.57993
	1852	2.2409	1.58304	7503	2.2821	1.57867
	2466	2.2454	1.58245	13722	2.3288	1.57411
	3698	2.2549	1.58161	33652	—	1.55897

Walls (1931) record  $\infty P_1$  in benzene at 25 °C as 177.1 and 161.1 c.c. respectively, while Briner *et al.* (1937) give  $\infty P_2$  in carbon tetrachloride at 23 °C as 174.6 and 144.7 c.c. The values presented by the former authors agree with ours, when allowance is made for the (small) solvent effect normally observed for the two media involved. The data published by Briner and collaborators are

somewhat low, possibly because their observations were taken at concentrations too great to permit accurate extrapolations of polarizations to infinite dilution.

The actual magnitudes of the polarities listed in Table 4 (dipole moments) display little dependence on molecular form: while the two maleates have slightly larger moments than their related fumarates the differences are too

TABLE 2  
LOSS TANGENT MEASUREMENTS IN CARBON TETRACHLORIDE AT 25 °C

Compound	$10^6 w_2$	$\Delta f$ (Mc/s)	$10^4 Q$	$10^4 \Delta \tan \delta'$
Dimethyl fumarate	0	1.97	6.32	—
	7684	3.00	9.64	39.84
	12121	3.55	10.76	53.28
	17508	4.13	13.27	83.40
	18695	4.56	14.65	99.96
Dimethyl maleate	0	2.19	7.04	—
	6759	2.90	9.31	27.24
	10205	3.26	10.49	41.40
	15101	4.08	12.90	70.32
Diethyl fumarate	0	1.72	5.33	—
	2453	2.21	7.11	18.96
	4248	2.41	7.75	26.64
	10092	3.52	11.32	69.48
	13958	4.24	13.63	97.20
	16166	4.56	14.66	109.2
Diethyl maleate	0	1.62	5.21	—
	7007	3.30	10.61	64.80
	13996	4.92	15.82	127.32
Diethyl azodiformate	0	1.84	5.92	—
	3458	2.31	7.43	18.12
	8171	3.21	10.32	52.80
	9020	3.24	10.42	54.00
	10404	3.40	10.93	60.12
	11160	3.43	11.03	61.32
Di- <i>n</i> -propyl azodiformate	0	1.72	5.52	—
	3524	2.93	9.42	46.68
	5876	3.42	10.99	65.52
	13054	4.66	14.98	111.4
	17494	6.20	20.26	176.8

small alone to justify allotment of configurations. Indeed, from their dipole moments one might conclude at first sight that all these diesters have much the same average disposition of their  $\cdot\text{CO}\cdot\text{OR}$  groups, each of which—following Marsden and Sutton (1936)—is internally “*trans*”, and presumably contributes a vector of *c.* 1.7 D acting roughly perpendicularly to the axis of the bond by which the  $-\text{CO}\cdot\text{OR}$  is attached to its neighbour atom.

TABLE 3  
 ELECTRIC DOUBLE REFRACTIONS IN CARBON TETRACHLORIDE AT 25 °C

Ethyl formate						
$10^3 w_2$	..	2335	3994	4450	5311	6676
$10^7 \Delta B$	..	0.162	0.281	0.313	0.371	0.465
$n_D$	..	—	—	—	—	1.4451
whence $10^7 \Delta B = 7.04_8 w_2 - 1.06 w_2^2$						
Diethyl oxalate						
$10^3 w_2$	..	519	2011	2396	2680	2936
$10^7 \Delta B$	..	0.019	0.057	0.073	0.075	0.079
$n_D$	..	1.4574	1.4561	1.4556	1.4555	1.4553
whence $10^7 \Delta B = 3.04_4 w_2 - 7.93 w_2^2$						
Dimethyl fumarate						
$10^3 w_2$	..	652	669	1132	1570	1823
$10^7 \Delta B$	..	0.030	0.032	0.050	0.065	0.084
$n_D$	..	1.4572	—	1.4573	1.4571	1.4569
whence $10^7 \Delta B = 4.50 w_2 - 4.1 w_2^2$						
Diethyl fumarate						
$10^3 w_2$	..	715	1371	2539	2852	2864
$10^7 \Delta B$	..	0.027	0.053	0.106	0.118	0.118
$n_D^*$	..	—	—	—	—	1.4564
whence $10^7 \Delta B = 3.70_7 w_2 + 15.3 w_2^2$						
Diethyl maleate						
$10^3 w_2$	..	397	1208	1715	2386	3418
$10^7 \Delta B$	..	0.004	0.028	0.031	0.039	0.066
$n_D^*$	..	—	—	—	—	1.4568
whence $10^7 \Delta B = 1.849 w_2 - 0.09 w_2^2$						
Diethyl azodiformate						
$10^3 w_2$	..	583	711	902	1116	1440
$10^7 \Delta B$	..	-0.012	-0.015	-0.017	-0.024	-0.028 <sub>5</sub>
$n_D^*$	..	—	—	—	1.4571	1.4569
whence $10^7 \Delta B = -2.11_4 w_2 + 7.8 w_2^2$						
Di-n-propyl azodiformate						
$10^3 w_2$	..	77	249	570	1135	2685
$10^7 \Delta B$	..	-0.002 <sub>5</sub>	-0.005	-0.012 <sub>5</sub>	-0.020 <sub>5</sub>	-0.051
$n_D^*$	..	—	—	—	—	1.4565
whence $10^7 \Delta B = -1.92_2 w_2 + 0.73 w_2^2$						

\*  $n_D$  for carbon tetrachloride = 1.4575.



The apparent relaxation times (Table 4) do not suggest any correlation with geometrical isomerism. Perhaps these are cases of "segment orientation" by twisting of the carbalkoxy-groups (cf. McGeer *et al.* 1952), although we note that when this occurs the di-derivative often has  $\tau$  notably less than that of the mono-derivative (e.g. aniline and *p*-phenylenediamine with  $\tau$ 's of 6.7 and less

TABLE 4

CALCULATION OF RESULTS: DIPOLE MOMENTS, RELAXATION TIMES, AND MOLAR KERR CONSTANTS

	$(\alpha\epsilon_1)_{w_2=0}$	$(\beta)_{w_2=0}$	$\infty P_2$ (c.c.)	$D^P$ (c.c.)	$\mu D$
Ethyl formate .. ..	9.58	-0.865	101.3 <sub>5</sub>	20.2*	2.0 <sub>1</sub>
Diethyl oxalate .. ..	7.41	-0.487	154.5	35.2†	2.4 <sub>1</sub>
Dimethyl fumarate .. ..	6.65	-0.414	138.8	35.6‡	2.2 <sub>5</sub>
Dimethyl maleate .. ..	8.04	-0.426	160.4	34.8†	2.4 <sub>8</sub>
Diethyl fumarate .. ..	6.29	-0.534	163.2	45.4†	2.4 <sub>9</sub>
Diethyl maleate .. ..	7.40 <sub>5</sub>	-0.480	181.8	44.7†	2.5 <sub>9</sub>
Diethyl azodiformate .. ..	7.19	-0.432	178.4	41.9†	2.5 <sub>8</sub>
Di- <i>n</i> -propyl azodiformate .. ..	7.21	-0.470	208.9	51.4†	2.7 <sub>7</sub>

	$\psi_{\text{mean}}$	$\tau \times 10^{12}$ (sec)
Dimethyl fumarate .. ..	0.493	8.5
Dimethyl maleate .. ..	0.433	4.8
Diethyl fumarate .. ..	0.685	13
Diethyl maleate .. ..	0.914	15
Diethyl azodiformate .. ..	0.584	9.0
Di- <i>n</i> -propyl azodiformate .. ..	0.104	17

	$\gamma$	$(\delta)_{w_2=0}$	$\infty ({}_m K_2) \times 10^{12}$
Ethyl formate .. ..	-0.124	100.7	54.6
Diethyl oxalate .. ..	-0.049	43.5	45.4
Dimethyl fumarate .. ..	-0.018	64.3	67.6
Diethyl fumarate .. ..	-0.027	53.0	66.5
Diethyl maleate .. ..	-0.016	26.4	31.5
Diethyl azodiformate .. ..	-0.027	-30.2	-41.9
Di- <i>n</i> -propyl azodiformate .. ..	-0.023	-27.5	-44.5 <sub>5</sub>

\* From Zahn (1932).

† Taken as  $1.05R_D$ ,  $R_D$ 's from Vogel (1948; see also Cresswell *et al.* 1952).‡  $1.05R_D$ ,  $R_D$  being estimated as  $R_{\text{diethyl fumarate}}$  minus  $2R_{\text{CH}_3}$ .

than  $1.5 \times 10^{-12}$  sec) while it is evident from the data listed by Smyth (1955) that the relaxation time of ethyl acetate is around  $2.2 \times 10^{-12}$  sec in heptane and c.  $4.4 \times 10^{-12}$  sec as a pure liquid.

The only physical property, among the three studied, in which diethyl maleate and fumarate differ markedly is therefore the molar Kerr constant; of the two, the latter has the greater  ${}_m K$ . Since, as explained elsewhere (Le

Fèvre and Le Fèvre 1953, 1955), the magnitude and algebraic sign of a molar Kerr constant depends upon two terms (the "anisotropy" and the "dipole" terms,  $\theta_1$  and  $\theta_2$  respectively), one of which ( $\theta_1$ ) is usually small and always positive, it appears likely that  $\theta_2$  for the fumarate exceeds that for the maleate.

Ethyl formate has been studied in an attempt to gain information on the last point. From the  $\infty(mK_2)$  and  $\mu$ , noted in Table 4, together with  $R_\infty$  (extrapolated from the refractivities listed by Vogel 1948a, 1948b; see also Jeffery and Vogel 1948), and the depolarization factor given by Cabannes (1929) for the liquid ester, we have:

$$\begin{aligned}b_1 + b_2 + b_3 &= 2.0600 \times 10^{-23}, \\2b_1 - b_2 - b_3 &= 2.3279_5 \times 10^{-24}, \\(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2 &= 0.0959 \times 10^{-46},\end{aligned}$$

whence

$$b_1 = 0.764 \times 10^{-23}, \quad b_2 = 0.755 \times 10^{-23}, \quad b_3 = 0.541 \times 10^{-23}.$$

Since the C—H link is isotropically polarizable

$$(b_L^{\text{CH}} = b_T^{\text{CH}} = b_V^{\text{CH}} = 0.063_5 \times 10^{-23}$$

(cf. Le Fèvre and Le Fèvre 1955), the semi-axes of the polarizability ellipsoid for the carboxy radical are:

$$b_1^1 = 0.700_5 \times 10^{-23}, \quad b_2^1 = 0.691_5 \times 10^{-23}, \quad b_3^1 = 0.477_5 \times 10^{-23}.$$

The orientation of  $b_1^1$ ,  $b_2^1$ , and  $b_3^1$  within the CO—OEt group seems likely to be such that  $b_2^1$  is approximately collinear with the bond joining R to COOEt in R·COOEt;  $b_1^1$  thus lies some 20–30° from the C=O direction.

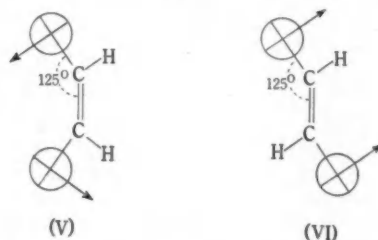
As a test of the foregoing we have made an *a priori* computation of the ellipsoid for diethyl oxalate, using  $b_1^1$ ,  $b_2^1$ , and  $b_3^1$ , in conjunction with the known ellipsoid for the C—C bond in cyclohexane ( $b_L^{\text{C—C}} = 0.098_6 \times 10^{-23}$ ,  $b_T^{\text{C—C}} = 0.027_4 \times 10^{-23}$ ). If the ellipsoids of the COOEt groups are joined, via a C—C bond, through their  $b_2^1$  directions, and the two  $b_1^1$  axes make azimuthal angles between 90 and 96°, then the calculated  $b$ 's for the oxalate molecule lead to  $mK_{\text{calc}}$  figures as follows:

$\alpha^\circ$	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$	$10^{35}(\theta_1 + \theta_2)$	$mK_{\text{calc.}} \times 10^{12}$
90	1.4194	1.4816	1.2054	12.33	51.85
92	1.4192	1.4816	1.2130	11.67	49.07
94	1.4188	1.4816	1.2210	10.95 <sub>5</sub>	46.06
96	1.4184	1.4816	1.2288	10.26	43.14

The  $\infty(mK_2)$  found by experiment is  $45.4 \times 10^{-12}$ ; accordingly our results indicate that the preferred azimuthal angle is around 95°. Such a conclusion is in agreement with the observed dipole moment of ethyl oxalate, and establishes confidence that our figures deduced for the anisotropy of CO<sub>2</sub>Et are not seriously in error.

We cannot proceed to a similar analysis of diethyl maleate or fumarate because, at present, convincing values for the semi-axes of polarizability for the C=C double bond are not available. Wang (1939), Denbigh (1940), and Bolton

(1954) have proposed that this link is equally polarizable in all transverse directions (i.e. that  $b_T = b_V$ , in the nomenclature of Le Fèvre and Le Fèvre 1955). Bolton, for example, calculates *from theory* that  $b_L^{C:C} = 0.286 \times 10^{-23}$  and  $b_T^{C:C} = b_V^{C:C} = 0.099 \times 10^{-23}$  e.e. We do not think that an equality between  $b_T$  and  $b_V$  is *a priori* probable, and experiments are proceeding on the point. Therefore, at this stage, we merely point out that the relative magnitudes of the molar Kerr constants of diethyl maleate and fumarate can be roughly forecast on extant data (taking the polarizability ellipsoid of the carboxy group as the same in maleates and fumarates as in ethyl formate, and that the ellipsoid of the C—C link in cyclohexane is applicable). Let their configurations be represented by V and VI respectively, in which the ellipsoids of  $\text{CO}_2\text{Et}$  are shown together with the



directions of action of  $\mu_{\text{CO}_2\text{Et}}$ . If V is nearly flat, the molecular resultant dipole moment will lie parallel to the C:C line, and (using Bolton's  $b_L^{C:C}$  and  $b_T^{C:C}$ ) the quantity  $2b_1 - b_2 - b_3$  (which practically controls the size of the molar Kerr constant) appears as  $0.215 \times 10^{-35}$ . In VI the molecular resultant will cross C:C at about 35° and  $2b_1 - b_2 - b_3$  emerges as  $0.515 \times 10^{-35}$ . Thus the ratio of  ${}_mK_{\text{maleate}}/{}_mK_{\text{fumarate}}$  is 1:2.4, while that observed is 1:2.2. Each of the  ${}_mK$ 's calculated from the figures just quoted are about twice those given in Table 4; they may be reduced by twisting the  $\text{CO}\cdot\text{OEt}$  groups so that their moments act above and below the  $\text{H}\cdot\text{C}:\text{C}\cdot\text{H}$  planes. As to the degrees of twist required to make calculation and observation agree, we prefer to defer further discussion until information is to hand on the polarizability ellipsoid of the carbon-carbon double bond.

Turning now to the case of diethyl azodiformate, and assuming that the geometry of the  $\text{C}\cdot\text{N}:\text{N}\cdot\text{C}$  portion is similar to that of  $\text{C}\cdot\text{CH}:\text{CH}\cdot\text{C}$  (cf. de Lange, Robertson, and Woodward 1939; Allen and Sutton 1950), we know from Hartley and Le Fèvre (1939) that in the *cis*- and *trans*-forms the  $\text{C}\cdot\text{N}:\text{N}\cdot\text{C}$  unit may contribute up to *c.* 3 and *c.* 0 D respectively to the resultant molecular dipole moment. The value observed for the azodiformate is actually 2.6 D. For a *trans*-azo configuration therefore the components from the two  $-\text{CO}\cdot\text{OEt}$  groups evidently cooperate: a model such as that envisaged for diethyl fumarate suggests itself. The possibility that the azodiformates are *cis*-structures cannot be discounted on present data, the probability is however small, since no stable *cis*-aliphatic azo-isomers have ever been isolated. If, then, diethyl azodiformate resembles in structure diethyl fumarate, the negativity of the  ${}_mK_2$  for the

former needs explanation. This cannot be ascribed to a greater non-planarity of the two carbethoxy groups, because then  $\mu_{\text{azodiformate}}$  should be less than  $\mu_{\text{fumarate}}$ , which is contrary to experience; more likely, it is due to the polarizability ellipsoid for  $\text{N}=\text{N}$  being markedly different from that for  $\text{CH}:\text{CH}$ .

However, as the literature contains no relevant information for the azo-link discussion cannot usefully be undertaken at present.

#### IV. ACKNOWLEDGMENTS

We have pleasure in recording our gratitude to the Commonwealth Government of Australia for a scholarship awarded to Wie Tat Oh under the Colombo Plan.

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## SPECTRA OF SULPHONYL DERIVATIVES\*

### III. INTERACTION WITH ATTACHED GROUPS

By D. E. FREEMAN† and A. N. HAMBLY†

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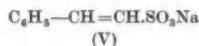
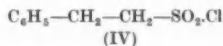
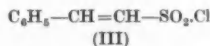
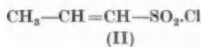
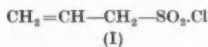
#### Summary

The Raman and infra-red spectra of 2-propene-1-sulphonyl chloride, 1-propene-1-sulphonyl chloride, 2-phenyl ethene and 2-phenyl ethane sulphonyl chlorides, and the infra-red spectrum of sodium 2-phenyl ethane sulphonate have been recorded. The constancy of sulphonyl, S—Cl, C—S, and C=C vibrations indicates the absence of conjugation in the ground state between C=C and S=O. The ultraviolet spectra of the styrene derivatives indicate a strong electronic interaction in the excited state. The 1-propene-1-sulphonyl chloride prepared by the method of Lambert and Rose (1949) is shown to be the *trans*-compound.

The constancy of the symmetric and asymmetric frequencies of the  $\text{SO}_3$  group in the ions  $\text{CH}_3\text{SO}_3^-$ ,  $\text{NH}_3\text{SO}_3^-$ , and  $\text{HOSO}_3^-$  also shows that there is no strong interaction between the lone pairs of electrons on the nitrogen or oxygen and the sulphur-oxygen  $\pi$ -bond system.

#### I. INTRODUCTION

In connection with a general study of the structure and reactivities of sulphonyl derivatives we have investigated the Raman and infra-red spectra of 2-propene-1-sulphonyl chloride (I), 1-propene-1-sulphonyl chloride (II), 2-phenyl ethene sulphonyl chloride (III), 2-phenyl ethane sulphonyl chloride (IV), and the infra-red spectrum of sodium 2-phenyl ethane sulphonate (V).



The Raman and infra-red spectra of sodium bisulphate, sodium sulphamate, and sodium methyl sulphonate have been remeasured and extended. Since our study was completed Simon and Kriegsmann (1956) have published a study of the Raman spectra of aqueous solutions of salts of methanesulphonic

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acid and Hoffmann and Andress (1956) have recorded the Raman spectrum of aqueous potassium sulphamate. Our results are in substantial agreement with these measurements.

## II. EXPERIMENTAL

### (a) Materials

(i) *2-Propene-1-sulphonyl Chloride*.—The Strecker reaction between aqueous sodium sulphite and allyl bromide (Belous and Postovskii 1951) yielded sodium 2-propene-1-sulphonate, which on treatment with phosphorus oxychloride gave I, b.p. 38 °C at 0.2 mm Hg.

(ii) *1-Propene-1-sulphonyl Chloride*.—Treatment of isopropanol with oleum (Lambert and Rose 1949) gave 1-propene-1-sulphonic acid, which was isolated as its barium salt. This salt was dehydrated with boiling toluene in a Dean-Stark apparatus and then treated with phosphorus oxychloride to give II, b.p. 52 °C at 0.4 mm Hg.

(iii) *2-Phenyl Ethene-1-sulphonyl Chloride*.—Sulphonation of styrene with sulphur trioxide in dioxan (Bordwell and Rondestvedt 1948) yielded 2-phenyl ethene-1-sulphonic acid, which was isolated as its sodium salt V. Treatment of the salt with phosphorus oxychloride gave III, which was purified by repeated crystallization from hexane, m.p. 88 °C.

(iv) *2-Phenyl Ethane-1-sulphonyl Chloride*.—The Strecker reaction of 2-phenyl ethyl bromide with aqueous sodium sulphite gave sodium 2-phenyl ethane-1-sulphonate, which on treatment with phosphorus pentachloride gave IV, b.p. 104 °C at 0.2 mm Hg; m.p. 33 °C.

(v) *Sodium Bisulphate*.—Analytical reagent  $\text{NaHSO}_4$  was recrystallized from its filtered aqueous solution and dried in a vacuum (Found: equiv. wt., 120. Calc. for  $\text{NaHSO}_4$ : equiv. wt., 121).

(vi) *Sodium Sulphamate*.—A filtered aqueous solution of sulphamic acid was titrated with a filtered aqueous solution of pure sodium hydroxide using phenolphthalein as external indicator. The solution was concentrated under reduced pressure (Found: S, 26.4; N, 11.9 per cent. Calc. for  $\text{NaSO}_3\text{NH}_2$ : S, 26.9; N, 11.8 per cent).

(vii) *Sodium Methane Sulphonate*.—Pure methyl methane sulphonate was saponified by shaking at room temperature with the stoichiometric quantity of filtered aqueous sodium hydroxide, and the water and methanol evaporated at reduced pressure (Found: S, 27.8; C, 10.6 per cent. Calc. for  $\text{NaSO}_3\text{CH}_3$ : S, 27.1; C, 10.2 per cent).

### (b) Apparatus

The infra-red spectra were determined on a Perkin-Elmer spectrometer modified by Walsh (1952) to a double monochromator, using sodium chloride and potassium bromide prisms.

The Raman spectra were excited by a Toronto type mercury arc, with the sample surrounded by filter solutions of either aqueous sodium nitrite or ethanolic solution of nitrobenzene (2 per cent.) and rhodamine 6 GDN (0.01 per cent.). The latter solution, which was circulated by means of a small centrifugal pump,

undergoes a slow change with loss of transmission at 4358 Å after exposure to the arc for several hours. The scattered spectrum was recorded on Kodak Super XX or Ilford Zenith plates with a Hilger Medium (E319) spectrograph, with glass optics, having a dispersion of  $17 \text{ Å mm}^{-1}$  at 4358 Å. Ultraviolet absorption spectra were measured with a Hilger Uvispek spectrophotometer.

### III. RESULTS

The Raman and infra-red spectra of the two propene sulphonyl chlorides, as determined on the pure liquids, are set out with approximate intensities and partial assignment of the frequencies in Table 1. The corresponding values for 2-phenyl ethene and 2-phenyl ethane sulphonyl chlorides are given in Table 3, while the resmaining results follow:

Sodium 2-phenyl ethane sulphonate: Infra-red spectrum of "Nujol" mull and mull in  $\text{C}_2\text{Cl}_4$  for regions in which "Nujol" absorbs: 543 m.\*, 562 m., 641 s., 693 m., 740 m., 744 m., 819 w., 866 w., 959 m., **1049†** m., 1068 vs., **1178** vs., **1198** m., 1227 vs., 1236 m., 1269 w., 1287 vw., 1306 w., 1324 w., 1450 w., 1495 w., 1624 w., 2930 w., 3055 w.

Sodium bisulphate: Raman spectrum of 7N aqueous solution: 427 m.br., 594 s.br., 893 m.br., 982 s. ( $\text{SO}_4$ ), **1051** vs., **1208** w.br.

Infra-red spectrum, "Nujol" mull: 577 s.; 606 m., 613 w.; 860 s., 873 s.; **1041** s., 1080 w.; **1173** s., **1240** m.; 1633 m., 3450 m.

Sodium sulphamate: Raman spectrum concentrated aqueous solution: 399 s., 565 s., 588 m.br., 816 m.br., 890 m.br., **1049** vs., 1117 w.br., **1194** m.br., 1250 w.br., 3237 m., 3420 m.

Infra-red spectrum, "Nujol" mull: 560 s., 565 s., 572 s.; 595 s.; 791 s.br., 885 m., 908 w.; **1056** s., **1069** s., **1081** s.; 1139 s., **1190** s., 1253 s., 1287 s.; 1583 m.; 3219 w., 3254 m.; 3312 m., 3382 w.

Sodium methane sulphonate: Raman spectrum, concentrated aqueous solution: 344 s., 531 s., 555 s., 787 vs., 968 m., **1050** vs., **1209** m.br., 1426 s., 2938 vs., 3023 s.

Infra-red spectrum, "Nujol" mull: 529 m., 535 s., 543 s.; 563 s.; 595 w., 618 m.; 780 m., 790 s., 796 m.; 964 vw., 991 vw.; **1051** s.; **1061** s., **1075** s., **1098** s., **1186** vs., 1199 vs.; 1253 w.

$\text{C}_2\text{Cl}_4$  mull: 2943 s., 3003 w., 3021 s.

### IV. DISCUSSION

#### (a) Propene Sulphonyl Chlorides

A comparison of the spectra of the two propene sulphonyl chlorides with those of related compounds (Sheppard and Simpson 1952; Ham and Hambly 1953a, 1953b) enables an assignment to be made for the majority of the frequencies (Table 1). The surprising constancy of the frequencies for the two

\* vs., very strong; s., strong; m., medium intensity; w., weak; vw., very weak; br., broad band.

† The characteristic frequencies associated with the bonds to the sulphur atom are indicated in bold face type.

TABLE I  
VIBRATIONAL FREQUENCIES OF PROPENE SULFONYL CHLORIDES

CH <sub>3</sub> ·CH:CH·SO <sub>2</sub> Cl		Assignment	CH <sub>2</sub> :CH·CH <sub>2</sub> SO <sub>2</sub> Cl		Assignment
Infra-Red Spectrum	Raman Spectrum		Infra-Red Spectrum	Raman Spectrum	
	186 m.			193 m.	
	290 s.			257 m. 295 m.	
	375 s.	S—Cl stretch		377 s.	S—Cl stretch
	411 w.			476 vw.	
519 m. 527 m.			518 w.		
539 s.	537 m.	SO <sub>2</sub> deformation	532 m.	539 m.	SO <sub>2</sub> deformation
570 } s. 578 }	573 m. br.		586 vw.		2 × 295 = 590
			618 m.	621 w.	
748 w.		2 × 375 = 750	637 m.	645 w.	C—H out-of-plane bend
763 m.	763 w.	C—S stretch	766 s.	767 s.	C—S stretch
808 s.	806 m.		872 m.		
947 s.			950 s.	951 w.	CH <sub>3</sub> out-of-plane deformation
979 vw.			988 m.	985 w.	C—H out-of-plane bend
1014 s.	1010 w.		1012 w.		
1033 m.	1030 vw.		1033 m.		
			1090 m.	1093 vw.	
1163 s.	1162 s.	SO <sub>2</sub> symmetric stretch	1169 s.	1165 s.	SO <sub>2</sub> symmetric stretch
1237 m.	1230 w.		1196 m.	1200 m. 1229 w.	
			1252 m.	1250 m.	



TABLE I (Continued)

CH <sub>3</sub> :CH:CH:SO <sub>2</sub> Cl		Assignment	CH <sub>2</sub> :CH:CH <sub>2</sub> SO <sub>2</sub> Cl		Assignment
Infra-Red Spectrum	Raman Spectrum		Infra-Red Spectrum	Raman Spectrum	
1299 m.	1297 m.	C—H in-plane deformation	1300 m.	1301 m.	—CH=C—deformation
1377 s.	1377 m.	SO <sub>2</sub> asymmetric stretch	1376 s.	1374 w.	SO <sub>2</sub> asymmetric stretch
				1402 m.	—CH <sub>2</sub> — deformation
1441 m.	1442 m.	CH <sub>3</sub> asymmetric deformation	1427 s.	1430 m.	=CH <sub>2</sub> in-plane deformation
1637 s.	1637 m.	C=C stretch	1640 m.	1642 s.	C=C stretch
2866 w.		CH <sub>3</sub> symmetric stretch			
2932 m.	2922 m.	CH <sub>2</sub> asymmetric stretch	2928 m.	2925 m.	CH <sub>2</sub> asymmetric stretch
3000 } m.	3044 w.	=C—H stretch	2996 m.	2996 } m.	—CH=CH <sub>2</sub> stretch
3073 }				3037 }	
			3092 w.	3106 w.	

SO<sub>2</sub> vibrations as well as those for C=C, C—S, and S—Cl indicates that there is no interaction between the electrons of the olefinic linkage and the attached sulphonyl chloride group in 1-propene-1-sulphonyl chloride. At most the effect of conjugation has just neutralized the difference in frequency for terminal and non-terminal olefinic bonds, and the increase in sulphone stretching frequencies due to the greater electronegativity of the *sp*<sup>2</sup> hybridized carbon atom attached to sulphur in II.

This is in agreement with the conclusion of Koch and Moffitt (1951) that there will be no appreciable conjugation unless two unsaturated centres are attached to the sulphur atom. On the other hand, Price and Gillis (1953) suggest that the absence of conjugation in methyl vinyl sulphone indicates that the sulphur and oxygen are joined by single dative bonds. Craig *et al.* (1954) have pointed out that, as the positive charge on the sulphur atom is increased, the outer 3*d* orbitals will become more concentrated and may strengthen the  $\sigma$ -bond system about sulphur by hybridizing with the 3*s* and 3*p* orbitals. This effect is probably responsible for the increase in the frequency of the C—S vibration in the series sulphide, sulfoxide, sulphonyl halide. A further exaltation of the C—S frequency is found in alkyl sulphonate ions (793 cm<sup>-1</sup> in methane

sulphonate) as a consequence of the spread of the  $d\pi$ ,  $p\pi$  orbitals over the three oxygen atoms despite the effect of the negative charge that is shared between them.

The contraction of the  $3d$  sulphur orbitals will increase the  $\pi$ -bond overlap with the  $2p$  orbitals of oxygen. This is reflected by the increased sulphur-oxygen stretching frequencies with attachment of electronegative groups (Table 2) and the changes produced by electron attracting *para*-substituents in aromatic sulphonic esters (Freeman and Hamby 1957).

TABLE 2  
VIBRATIONAL FREQUENCIES OF  $\text{SO}_2$  GROUP

Compound	$>\text{SO}_2$ Symmetric Stretch ( $\text{cm}^{-1}$ )	$>\text{SO}_2$ Asymmetric Stretch ( $\text{cm}^{-1}$ )	$>\text{SO}_2$ Deformation ( $\text{cm}^{-1}$ )
$\text{CH}_3\text{SO}_2\text{C}_3\text{H}_7^{(a)}$ .. ..	1139	1308	—
$\text{C}_6\text{H}_5\text{SO}_2\text{C}_6\text{H}_5^{(b)}$ .. ..	1144	1336	—
$\text{CH}_3\text{SO}_2\text{Cl}^{(c)}$ .. ..	1168	1361	531
$\text{C}_6\text{H}_5\text{SO}_2\text{Cl}^{(d)}$ .. ..	1184	1375	575
$\text{CH}_3\text{SO}_2\text{F}^{(e)}$ .. ..	1186	1401	538
$\text{C}_6\text{H}_5\text{SO}_2\text{F}^{(d)}$ .. ..	1179	1409	588
$\text{ClSO}_2\text{Cl}^{(e)}$ .. ..	1205	1434	563
$\text{ClSO}_2\text{F}^{(f)}$ .. ..	1211	1447	—
$\text{FSO}_2\text{F}^{(f)}$ .. ..	1263	1497	547

<sup>(a)</sup> Price and Gillis (1953); <sup>(b)</sup> Barnard, Fabian, and Koch (1949);  
<sup>(c)</sup> Ham and Hamby (1953a); <sup>(d)</sup> Ham and Hamby (1953b); <sup>(e)</sup> Martz and  
 Lagemann (1954); <sup>(f)</sup> Bender (personal communication).

Such overlap of a diffuse  $3d$  orbital would not be critically dependent on angular arrangement, and consequently the  $\text{SO}_2$  deformation frequency does not strictly follow the variation in the stretching frequencies. The multiple frequencies in the region of the  $\text{SO}_2$  deformation vibration may indicate the presence of rotational isomerism about the CS bond, particularly in 1-propene-1-sulphonyl chloride, in which models indicate close approach between the  $\alpha$ - and  $\beta$ -hydrogen atoms and the atoms attached to sulphur. We are at present investigating such a case in  $\alpha$ -halogen substituted sulphonyl derivatives.

Price and Gillis (1953) show that in the change from sulphoxide to sulphone there is little change in electron polarizability as evidenced by the calculated bond refractions and they use this as an argument against the multiple character of the sulphur-oxygen bonds. The intensity of the  $\text{SO}_2$  symmetrical stretching frequency, which in the Raman spectra of both propene sulphonyl chlorides is similar to that of the olefinic bond, shows the large change of polarizability with bond length that is characteristic of multiple bonds.

From the interatomic distances concerned, it could be predicted that the *trans*-form of 1-propene-1-sulphonyl chloride would be much more stable than the *cis*-form. The existence of only one olefinic stretching frequency in the

TABLE 3

VIBRATIONAL SPECTRA 2-PHENYL ETHENE AND 2-PHENYL ETHANE SULFONYL CHLORIDES

$C_6H_5CH : CHSO_2Cl$		$C_6H_5CH_2CH_2SO_2Cl$		Assignment
Infra-Red Spectrum "Nujol" Mull	Raman Spectrum $CHCl_3$ Solution	Infra-Red Spectrum	Raman Spectrum Liquid	
	209 w.		204 s.	
	235 m.		239 m.	
	264 ( $CHCl_3$ )		261 w.	
		•	291 s.br.	$C_6H_5CH_2CH_2$ skeletal
	311 vw.			
	376 ( $CHCl_3$ )			
	382 s.		374 vs.	S—Cl stretch
	459 w.br.	Liquid film		
	493 w.br.			
516 vs.	517 s.	507 s.	504 m.	
566 s.	568 vs.	535 vs.	539 s.	$SO_2$ deformation
		585 m.	584 m.	
611 s.	626 s.	610 m.	618 s.	Aromatic C—C—C in-plane bend
687 w.	675 ( $CHCl_3$ )	699 s.	699 m. }	C—H out-of-plane deformation
745 s.		737 s.	737 s. }	
(806 m.)	765 m.v.br.	763 vs.	763 s.	C—S stretch
821 s.	820 vs.	"Nujol" mull	833 vs.	
860 s.	866 s.	914 w.	914 w.br.	
979 m.	978 vw.	976 w.		
990 w.				
999 vw.	1009 s.	1006 w.	1004 vs. }	Aromatic ring vibrations
1028 vw.	1035 w.	1032 w.	1033 s. }	
1073 vw.		1055 vw. 1072 vw.		

TABLE 3 (Continued)

$C_6H_5CH:CHSO_2Cl$		$C_6H_5CH_2.CH_2SO_2Cl$		Assignment
Infra-Red Spectrum "Nujol" Mull	Raman Spectrum $CHCl_3$ Solution	Infra-Red Spectrum	Raman Spectrum Liquid	
1099 w.		1106 vw.		
1118 w.	1132 vw.			
1161 s.	1170 m.	1153 s.		
1185 w.	1189 s.	1169 s.	1163 vs.	SO symmetric stretch
1201 w.	1201 vw.	1181 m.	1203 s.	
		1224 vw.		
1294 w.	1248 s.vbr.	1264 w.	1239 w.	
1310 w.	1310 w.	1321 w.		
1335 m.	1340 m.	1339 s.	1341 w.	
1371 s.	1382 w.	1363 vs.	1374 m.	$SO_2$ asymmetric stretch
	1391 vw.		1401 m.	
1453 m.	1457 m.		1453 m.br.	
1498 w.	1506 w. 1554 vw.			
1577 m.	1581 s.	$C_2Cl_4$ solution	1588 m.	Aromatic
1610 m.	1603 vs. 1624 s.		1604 s.	Aromatic
		2859 } w. 2883 }		$>C=C<$
		2932 w.	2920 s.	$CH_2$ stretch
3054 w.	3043 w.	3043 } w. 3075 }	3058 s.	Aromatic CH stretch
3096 w.	3065 w.			$=CH$ stretch

vibration spectrum indicates that the preparation we have used yields predominantly a single product. That this is the *trans*-form is confirmed by the occurrence of the CH, in-plane, deformation with medium intensity in both Raman and infra-red spectra at  $1298\text{ cm}^{-1}$  and the CH out-of-plane vibration in absorption at  $947\text{ cm}^{-1}$ . The *cis*-form is expected to have frequencies of  $1260$  and  $\sim 690\text{ cm}^{-1}$  (Sheppard and Simpson 1952).

(b)  *$\omega$ -Styrene Derivatives*

These compounds do not permit the same unambiguous assignment of frequencies as the propene sulphonyl chlorides. The differences between some of the infra-red and Raman frequencies for 2-phenyl ethene-1-sulphonyl chloride are due to the use of a 3M chloroform solution for the Raman spectrum. The overlap of the very strong chloroform vibration at  $370\text{ cm}^{-1}$  may also have given a slight displacement to the S—Cl peak at  $382\text{ cm}^{-1}$  in the microphotometer trace of the Raman spectrum. The difference between the S—Cl frequencies of the saturated and unsaturated sulphonyl chlorides may thus be exaggerated. All others of the 12 sulphonyl chlorides we have studied have this frequency in the range  $369\text{--}377\text{ cm}^{-1}$ .

In the saturated 2-phenyl ethene-1-sulphonyl chloride, the frequencies  $1163$  (Raman, liquid) and  $1169$  (infra-red, solid) can be assigned to the symmetrical  $\text{SO}_2$  stretch. Of the three absorptions  $1153$ ,  $1169$ ,  $1181$ , the first and last have counterparts ( $1155$ ,  $1180$ ) in the infra-red spectrum of ethyl benzene (Pitzer and Scott 1943). The corresponding asymmetric frequencies  $1374$ ,  $1363\text{ cm}^{-1}$  are only slightly lower than those of the propene sulphonyl chlorides. Ethyl benzene shows only one weak Raman line ( $550\text{ cm}^{-1}$ ) in the range  $500\text{--}600\text{ cm}^{-1}$ , so that the presence of three Raman and infra-red bands  $506$ ,  $537$ ,  $584\text{ cm}^{-1}$  in the sulphonyl chloride may again be due to the splitting of the  $\text{SO}_2$  deformation frequency due to rotational isomerism.

With 2-phenyl ethene-1-sulphonyl chloride and the corresponding sodium sulphonate we are unable to assign frequencies characteristic of either  $\text{SO}_2$  deformation or C—S stretching owing to the occurrence of vibrational frequencies of styrene (Pitzer, Guttman, and Westrum 1946) in the same regions. In the sulphonyl chloride the strong adsorption at  $1371\text{ cm}^{-1}$  corresponding to the weak Raman band at  $1382\text{ cm}^{-1}$  in chloroform solution is the asymmetric  $\text{SO}_2$  stretch, while the symmetrical mode is given by  $1189$ ,  $1185\text{ cm}^{-1}$ , stronger in scattering than in absorption, rather than  $1170$ ,  $1161\text{ cm}^{-1}$  where the reverse intensity ratio is found. Williams (1936) did not observe  $1180\text{ cm}^{-1}$  in styrene absorption, and Lespieau and Bourguet (1930) found the corresponding Raman band to be very weak. The small increases in frequency between phenyl ethane and phenyl ethene sulphonyl chlorides are to be attributed to the greater electronegativity of the  $sp^2$  hybridized carbon atom compared to the  $sp^3$  hybridized carbon atom attached to the sulphur in the saturated compound. We had expected similar small differences between the two propene sulphonyl chlorides but, as in the comparison between allyl methyl sulphone and vinyl methyl sulphone (Price and Gillis 1953), the differences were not significant. We conclude that in sulphonyl chlorides, for which the double-bond character

of the sulphur-oxygen linkage is strongly developed, no conjugation with an olefinic bond occurs.

The symmetry about the sulphur atom is different in sodium 2-phenyl ethene sulphonate, for which the absorptions 1049, 1068 are associated with the symmetric  $\text{SO}_3$  stretching vibration and 1178, 1198 with the asymmetric stretch. In crystalline sodium methane sulphonate the corresponding frequencies are grouped about  $1060\text{ cm}^{-1}$  and at 1186, 1199. Again there is no evidence for significant modification of the SO frequencies due to conjugation with the olefinic bond.

Although the vibrational frequencies of the ground states of the  $\omega$ -styrene derivatives are normal, the ultraviolet absorption spectra, determined for 2-phenyl ethene sulphonyl chloride in hexane solution and for sodium 2-phenyl ethene sulphonate in aqueous solution, indicate a strong interaction with the mobile  $\pi$ -electrons of the conjugated styrene system (Table 4). The saturated

TABLE 4  
VALUES OF  $\lambda_{\text{max}}$  (Å) AND LOG  $\epsilon_{\text{max}}$ .  
Log  $\epsilon_{\text{max}}$  is shown in parentheses

$\text{C}_6\text{H}_5\cdot\text{C}_2\text{H}_5$ Jones (1943)	$\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}_2$ Hirschberg (1949)	$\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{CH}_3$ Hirschberg (1949)	$\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{SO}_2\text{Cl}$	$\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{SO}_3^-$
2060 (4.5)			2205 (3.8)	2160 (4.2)
2590 (2.2)	2440 (4.2) 2730 (2.9) 2820 (2.9)	2460 (4.3)  2840 (3.0)	2750 (4.3)	2565 (4.3)

alkyl sulphones are transparent for wavelengths greater than  $1800\text{ Å}$ , but an attached sulphonate group has a marked effect on the benzene absorption spectrum (Matsen 1956). The ultraviolet absorption spectra of allyl benzene, ethyl benzene, and dibenzyl sulphone are similar, but differ from those of styrene and  $\omega$ -methyl styrene, which in turn resemble one another. The marked change produced when the  $\text{SO}_2\text{Cl}$  and  $\text{SO}_3^-$  groups are in the terminal position indicates that, as the bond orders are normal in the ground state, there must be strong interaction in the excited electronic state.

(c) *The  $\text{X}\cdot\text{SO}_3^-$  Ions*

The spectra of the  $\text{XO}_3^-$  ions ( $\text{X}=\text{OH}$ ,  $\text{NH}_2$ ,  $\text{CH}_3$ ) have been reported previously. For sodium bisulphate, our results agree with previous investigators (Nisi 1929; Shaffer and Cameron 1936), who however have not found the Raman line at 1208, which we believe to be the  $\text{SO}_3^-$  asymmetric stretch. Our infra-red spectrum agrees with but extends into the KBr region, the study of Miller and Wilkins (1952). We are in general agreement with the recent assignments of Simon and Kriegsmann (1956) for sodium methane sulphonate and

with the assignments of the symmetrical and asymmetrical  $\text{SO}_3^-$  vibrations in the sulphamate ion by Hofmann and Andress (1956). The allotment of  $\sim 545 \text{ cm}^{-1}$  as the S—N stretching frequency by the latter workers seems to us to be improbable. Their decision is based on the relative constancy of such a frequency in a series of compounds with nitrogen attached to  $\text{SO}_2$  or  $\text{SO}_3^-$  and a calculation using an assumed force constant for the sulphur-nitrogen bond. In those compounds which they considered, where there is more than one  $\text{SO}_3^-$  group attached to the same nitrogen atom, there is an appreciable elevation of the  $\text{SO}_3^-$  stretching frequencies and the interaction through nitrogen in such compounds must be strong. This would be expected to alter the S—N vibration frequency. It is probable that this frequency in sulphamates lies between that of C—S in methane sulphonates ( $787 \text{ cm}^{-1}$ ) and of S—OH in bisulphates ( $893 \text{ cm}^{-1}$ ), and we therefore consider that the medium intensity Raman band corresponding to the strong absorption at  $791 \text{ cm}^{-1}$  in the crystal is the more likely value for this stretching frequency. The frequencies  $565$  and  $588 \text{ cm}^{-1}$  are assigned to the asymmetric and symmetric  $\text{SO}_3^-$  bending frequencies since the second is stronger in the Raman spectrum, while the total intensity of the group centred at  $565$  in the infra-red is much higher than that at  $595 \text{ cm}^{-1}$ .

The  $\text{SO}_3^-$  stretching frequencies in the ions we have studied, again show a surprising constancy independent of the availability of electrons on the other atom attached to sulphur. We infer that there is no tendency for these atoms to become involved in the system of  $\pi$ -bonds about the sulphur atom. However, this behaviour is not completely general, for when two or more  $\text{SO}_3^-$  groups are joined to the same nitrogen atom (Hofmann and Andress 1956) or  $\text{SO}_3^-$  to an S atom in thiosulphate ion (Siebert 1954), the frequencies are considerably modified.

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## SPECTRA OF SULPHONYL DERIVATIVES

### IV. SULPHONIC ESTERS

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#### Summary

The symmetric and asymmetric  $\text{SO}_2$  stretching frequencies ( $1190, 1365 \text{ cm}^{-1}$ ) and the  $\text{SO}_2$  deformation frequency ( $565 \text{ cm}^{-1}$ ) in esters of arylsulphonic acids are similar to those for sulphonyl chlorides. A frequency of about  $800 \text{ cm}^{-1}$  can be correlated with the presence of the  $\text{SO}_2\text{OR}$  group and is probably the S—OR bond stretching vibration. The corresponding frequencies in methyl methane sulphonate are slightly lower. A doubling of some frequencies is attributed to the occurrence of rotational isomerism in the sulphonic ester group.

The frequency noted by Ham and Hambly (1953b) and suggested as characteristic of aromatic sulphonyl derivatives corresponds to a very constant vibration  $1095\text{--}1099 \text{ cm}^{-1}$  in the aromatic esters studied.

### I. INTRODUCTION

The authors have investigated the infra-red and Raman spectra of seven sulphonic esters in order to find if the alkoxy group is involved in the  $\pi$ -bond system about the sulphur atom. They have also taken the opportunity to show which frequencies are characteristic of the sulphonate esters.

### II. EXPERIMENTAL

#### (a) Materials

The sulphonate esters were prepared (Table 1) by the dropwise addition of the sodium alkoxide to a stirred solution of the corresponding pure sulphonyl chloride or fluoride in the alcohol or an alcohol-chloroform mixture. On dilution with water the sodium halide dissolved, the ester was separated, dried over anhydrous magnesium sulphate, and purified by at least two distillations under reduced pressure. For the preparation of the methyl *o*-toluene sulphonate, *o*-toluene sulphonyl fluoride which had been purified by the method of Davies and Dick (1931) was used to ensure freedom from the *para*-isomer. It was found that, if esters containing a trace of the sulphonyl chloride were used, a turbidity appeared during exposure to the mercury arc.

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## (b) Apparatus

The infra-red and Raman spectra were recorded with the apparatus described in Part III of this series (Freeman and Hamby 1957) except the infra-red spectra at frequencies above  $1200\text{ cm}^{-1}$  have recently been re-examined at higher resolution using a calcium fluoride prism in a double-pass spectrometer.

TABLE I  
PREPARATION OF SULPHONIC ESTERS

Sulphonyl Halide	Solvent	Sulphonic Ester	B.p. or M.p.
$\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ .. ..	$\text{CH}_3\text{OH}$	$\text{C}_6\text{H}_5\text{SO}_2\text{OCH}_3$	$120^\circ\text{C}/1.2\text{ mm}$
$\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ .. ..	$\text{C}_2\text{H}_5\text{OH}$	$\text{C}_6\text{H}_5\text{SO}_2\text{OC}_2\text{H}_5$	$141^\circ\text{C}/1\text{ mm}$
$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$ ..	$\text{CH}_3\text{OH}$	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{OCH}_3$	M.p. $28^\circ\text{C}$
$o\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{F}$ ..	$\text{CH}_3\text{OH}$	$o\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{OCH}_3$	$162^\circ\text{C}/10\text{ mm}$
$p\text{-BrC}_6\text{H}_4\text{SO}_2\text{F}$ .. ..	$\text{CH}_3\text{OH}/\text{CHCl}_3$	$p\text{-BrC}_6\text{H}_4\text{SO}_2\text{OCH}_3$	M.p. $60^\circ\text{C}$
$p\text{-NO}_2\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$ ..	$\text{CH}_3\text{OH}/\text{CHCl}_3$	$p\text{-NO}_2\text{C}_6\text{H}_4\text{SO}_2\text{OCH}_3$	M.p. $88^\circ\text{C}$
$\text{CH}_3\text{SO}_2\text{Cl}$ .. ..	$\text{CH}_3\text{OH}$	$\text{CH}_3\text{SO}_2\text{OCH}_3$	$59^\circ\text{C}/0.6\text{ mm}$

## III. RESULTS AND DISCUSSION

## (a) Methyl Methane Sulphonate

Since our study was completed, Simon, Kriegsmann, and Dutz (1956) have published measurements of the Raman spectra of methyl methane sulphonate and ethyl methane sulphonate. These are compared with the results presented in Table 2.

The comparison of the vibration spectrum of methyl methane sulphonate with that of methane sulphonyl chloride, for which we have recently obtained improved values of the infra-red C—H stretching frequencies, enables an assignment to be made for the major frequencies.

The  $\text{SO}_2$  stretching frequencies, the asymmetric at  $1354\text{ cm}^{-1}$  and the symmetric at  $1165\text{ cm}^{-1}$ , are the strongest bands in the infra-red and Raman spectra respectively and are only slightly lower than those for the corresponding sulphonyl chloride. This slight change is to be attributed to the lower electro-negativity of the methoxy group compared to the chlorine atom. If the oxygen of the methoxy group were involved to an appreciable extent in the  $\pi$ -bond system of the other sulphur-oxygen linkages, a pronounced lowering of frequency would occur towards the values  $1210, 1050\text{ cm}^{-1}$  characteristic of the sulphonate ion.

For a film of the pure liquid, the  $\text{SO}_2$  asymmetric stretch is represented by an intense, broad, infra-red band at  $1353\text{ cm}^{-1}$  on which the symmetrical methyl vibration ( $1327\text{ cm}^{-1}$ ) appears as a well-defined shoulder. The ester is only slightly soluble in non-polar solvents, indicating a strong interaction between the ester molecules. When the saturated solution of the ester in tetrachloroethylene is examined, the removal of the perturbation due to this strong inter-molecular attraction causes the centre of the band to move to  $1363\text{ cm}^{-1}$  while the absorption splits into two sharper bands at  $1373$  and  $1353\text{ cm}^{-1}$  (Fig. 1). This behaviour could be due to either rotational isomerism about the S—OMe

TABLE 2  
VIBRATIONAL SPECTRA OF METHANESULFONIC ACID DERIVATIVES

$\text{CH}_3\text{SO}_3\text{OCH}_3^{\text{II}}$				$\text{CH}_3\text{SO}_3\text{Cl}$		$\text{CH}_3\text{SO}_3\text{OC}_2\text{H}_5$	Assignment
Infra-Red Spectrum Present Work	Infra-Red Spectrum Simon, Kriegsmann, and Dutz (1956)	Raman Spectrum Present Work	Raman Spectrum Simon, Kriegsmann, and Dutz (1956)	Infra-Red Spectrum Ham and Hamby (1953a), Present Work	Raman Spectrum Ham and Hamby (1953a)	Raman Spectrum Simon, Kriegsmann, and Dutz (1956)	
			271 w.		216 w. 257 m. 288 m.		
		263 m.	328 w.		(377 vs. S-Cl)	340 m.	
		328 s.	345 m.	490 s.	486 s.	467 m.	
		338 s.	469 s.	528 m.	538 s.br.	531 s. 553 w.	SO <sub>2</sub> deformation
529 s.		465 vs.	530 s.				
549 w.		524 vs.	555 w.				
		548 s.		751 s.	748 m.	717 m. 737 s.	C-S stretch
723 m.		724 vs.	727 vs.				
		813 s.	817 m.		(811 w.)	798 w. 819 m.	S-OMe stretch
816 s.							
972 s.		974 s.	974 w.	968 s.	966 w.	919 vw. 974 w.	? CH <sub>3</sub> wag
						1010 w.	
1002 s.	Band 971-1010	995 m.	1001 w.				

TABLE 2 (Continued)  
VIBRATIONAL SPECTRA OF METHANE SULFONIC ACID DERIVATIVES

$\text{CH}_3^{\text{I}}\text{SO}_3\text{OCH}_3^{\text{II}}$				$\text{CH}_3\text{SO}_2\text{Cl}$		$\text{CH}_3\text{SO}_2\text{OC}_2\text{H}_5$	Assignment
Infra-Red Spectrum Simon, Kriegsmann, and Dutz (1956)	Infra-Red Spectrum Simon, Kriegsmann, and Dutz (1956)	Raman Spectrum Present Work	Raman Spectrum Simon, Kriegsmann, and Dutz (1956)	Infra-Red Spectrum Ham and Hamby (1953a), Present Work	Raman Spectrum Ham and Hamby (1953a)	Raman Spectrum Simon, Kriegsmann, and Dutz (1956)	
1060 vw.						1106 m.	$\text{SO}_2$ symmetric stretch
1176 s.	1176 vs.	1165 vs.	1171 vs.	1175 vs.	1168 vs.	1172 vs.	$\text{CH}_3^{\text{I}}$ symmetric deform.
1327 m.	1333 vs.	1330 shoulder		1320 s.			$\text{SO}_2$ asymmetric stretch
1353 vs.	1370 vs.	1354 m.	1358 w.	1367 vs.	1361 m.br.	1352 w.	$\text{CH}_3^{\text{I}}$ asymmetric deform.
1416 m.	Band 1449-1471 w.	1414 s.	1420 w.	1410 m.	1409 m.br.	1456 m.br.	$\text{CH}_3^{\text{II}}$ symmetric stretch
1461 s.		1455 m.	1464 w.				$\text{CH}_3^{\text{I}}$ symmetric stretch
2849 v.w.			2849 w.				$\text{CH}_3^{\text{II}}$ asymmetric stretch
2944 w.		2936 vs.	2944 s.	2935 m.	2933 s.	(2942 vs.)	$\text{CH}_3^{\text{I}}$ asymmetric stretch
2964 m.		2956 s.	2969 m.			(2986 m.)	$\text{CH}_3^{\text{II}}$ asymmetric stretch
3027 s.	3030 m.	3023 s.	3030 m.	{ 3021 s. 3043		(3028 m.)	$\text{CH}_3^{\text{I}}$ asymmetric stretch

bond which can give rise to two stereoisomeric *gauche* forms and a *trans*-form (Fig. 2), or to a Fermi resonance between the  $\text{SO}_2$  asymmetric stretching frequency and a combination band  $813 + 548 = 1361 \text{ cm}^{-1}$ .

The following tests favour the first alternative. A solution of methyl methane sulphonate in chloroform has the band centre close to that for the pure liquid but the intensities of the two constituent absorptions are now very

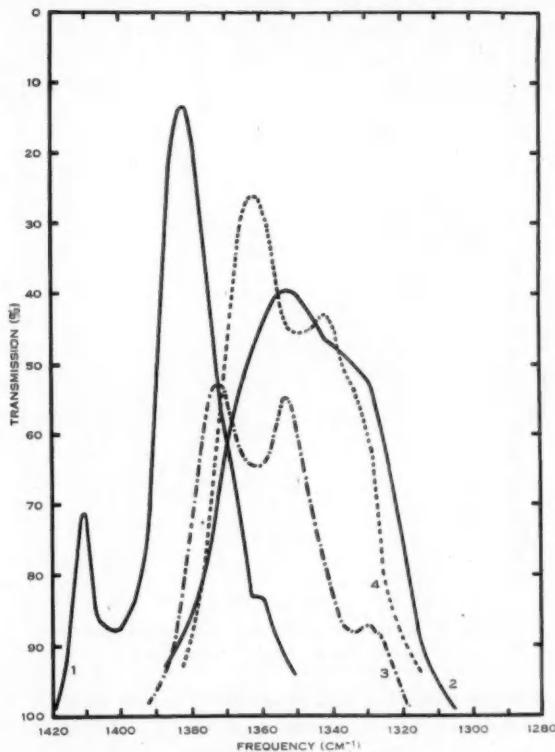


Fig. 1.—Asymmetric  $\text{SO}_2$  stretching band.

- 1, Full line (left): Methane sulphonyl chloride in  $\text{C}_2\text{Cl}_4$ .
- 2, Full line (right): Methyl methane sulphonate (thin liquid film).
- 3, — — — Methyl methane sulphonate (saturated solution in  $\text{C}_2\text{Cl}_4$ ).
- 4, - - - - Methyl methane sulphonate (dilute solution in  $\text{CHCl}_3$ ).

different from those in a non-polar solvent. Barnard, Fabian, and Koch (1949) have attributed the shift in the sulphonyl absorption frequencies to lower values, when the solvent is changed from carbon tetrachloride to chloroform, as due to hydrogen-bond formation between the latter solvent and the sulphonyl oxygen atoms. There is a similar more pronounced change with carbonyl compounds. If this action occurs more readily with the sulphonyl than the methoxy-oxygen,

the interaction would be expected to favour the *gauche* forms. If the isomeric forms absorb equally, then the relative intensities in the tetrachloroethylene solution indicate that there is an energy factor favouring the *trans*-form sufficient almost to balance the statistical advantage of the *gauche* form. The rapid adjustment of the equilibrium on change of solvent indicates that there is only a small energy barrier between the various forms.

The methyl esters of aromatic sulphonic acids all show two absorptions, with a separation of about  $22\text{ cm}^{-1}$ , at about  $1370\text{ cm}^{-1}$  in dilute tetrachloroethylene solution (Fig. 3), and these move together to lower frequencies ( $\Delta \sim 13\text{ cm}^{-1}$ ) in chloroform solution or in the pure ester. Adjacent frequencies

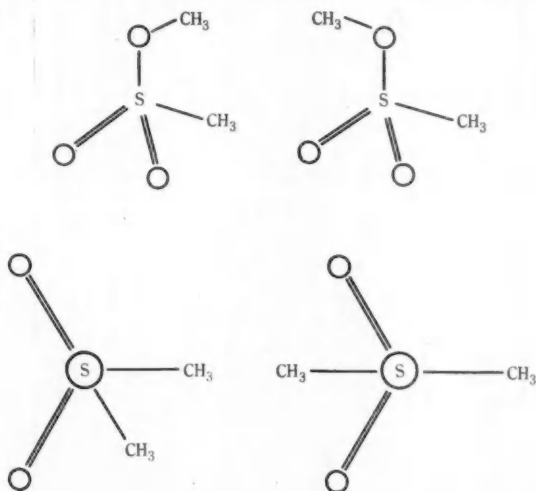


Fig. 2.—Elevation and plan of methyl methane sulphonate molecule.  
Left: *gauche* form. Right: *trans*-form.

show only minor shifts with this change of solvent. The effect is obscured in methyl *p*-nitrobenzene sulphonate because of a coincidence with the symmetric stretching frequency of the nitro group. In the case of the aromatic esters the form (*gauche*?) absorbing at higher frequencies seems to be at a higher concentration.

There are two absorptions in the region of the  $\text{SO}_2$  deformation frequency in methyl methane sulphonate and several of the other esters. Simon, Kriegsmann, and Dutz (1956) have attributed these to the two types of  $\text{SO}_2$  deformation involving the sulphonyl- and methoxy-oxygen atoms. The two frequencies may alternatively represent those of the two rotational isomers, with the deformation frequency involving the methoxy group at a much lower frequency ( $340\text{ cm}^{-1}$ ?).

The assignment of the methyl frequencies is assisted by the comparison with methane sulphonyl chloride. The methyl group attached to sulphur will

be referred to as  $\text{CH}_3^{\text{I}}$ , while that attached to oxygen will be  $\text{CH}_3^{\text{II}}$ . In methane sulphonyl chloride the  $\text{CH}_3^{\text{I}}$  asymmetric stretching frequency is raised from the value  $2962\text{ cm}^{-1}$  of paraffins to  $3031\text{ cm}^{-1}$ , while the symmetrical stretching frequency increases from the "paraffin" value of  $2872$  to  $2935\text{ cm}^{-1}$ . At the

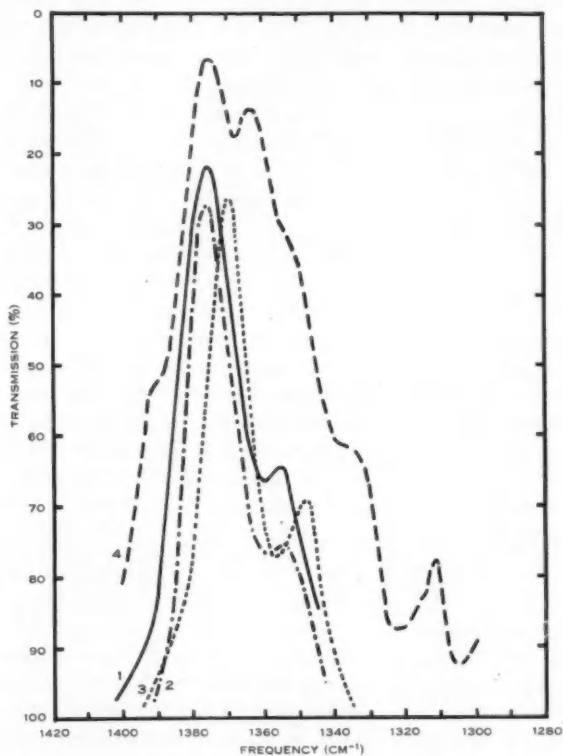


Fig. 3.—Asymmetric  $\text{SO}_2$  stretching band in  $\text{C}_2\text{Cl}_4$  solution.

- 1, Full line: Methyl benzene sulphonate.
- 2, — — — Methyl *p*-toluene sulphonate.
- 3, - - - - Methyl *o*-toluene sulphonate.
- 4, — · — Ethyl benzene sulphonate.

(The structures at  $1392, 1363\text{ cm}^{-1}$  are due to the ethyl group of the ester, which is at much higher concentration than the methyl esters.)

same time the methyl asymmetric and symmetric bending frequencies are displaced downwards from the paraffin values of  $1460, 1380\text{ cm}^{-1}$  to  $1410, 1320\text{ cm}^{-1}$ . Similar values have been reported recently by Simon and Kriegsmann (1956) for the methyl frequencies in methanesulphonic acid and its anhydride. This enables us to distinguish the vibrations of the two methyl

groups in the ester from one another. Those at 3027, 2944, 1416, and 1327  $\text{cm}^{-1}$  are due to  $\text{CH}_3^{\text{I}}$ , while the frequencies at 2964, 2849, and 1461  $\text{cm}^{-1}$  are due to  $\text{CH}_3^{\text{II}}$ . We have not observed an absorption (expected at  $\sim 1380 \text{ cm}^{-1}$ ) for the  $\text{CH}_3^{\text{II}}$  symmetrical bend. In the aromatic sulphonic esters the  $\text{CH}_3^{\text{II}}$  frequencies are all at 2954–2956  $\text{cm}^{-1}$  and 2842–2845  $\text{cm}^{-1}$  for the asymmetric and symmetric stretching vibrations. The very high intensity of 2936 in the Raman spectrum of the aliphatic ester compared to 2956 and 3023  $\text{cm}^{-1}$  indicates that it is a symmetrical vibration. The frequencies of  $\text{CH}_3^{\text{II}}$  can thus be described as normal, but those of  $\text{CH}_3^{\text{I}}$  are modified by attachment to the strongly electronegative sulphonyl group. The modification can be interpreted in terms of uneven  $sp^3$  hybridization of the carbon orbitals. The positive charge developed on the sulphur atom by the attachment of several electronegative atoms favours a displacement of electrons, in the C–S bond, towards sulphur. This will be more effective if these electrons remain in an orbital with more  $p$  character and hence more polarizable. In the limit, with the complete transfer of these electrons, the  $\text{CH}_3^{\text{I}}$  group would transform to a planar  $\text{CH}_3^+$  ion with  $sp^2$  hybridization. The increase in  $s$  character of the CH bonds will simultaneously shorten and strengthen them but make them less dependent on angular position, so that the deformation frequencies will decrease while the stretching frequencies increase. However, the attack of nucleophilic reagents ( $\text{H}_2\text{O}$ ,  $\text{OH}^-$ ,  $\text{OR}^-$ ) is at  $\text{CH}_3^{\text{II}}$ , which has normal frequencies and is apparently less electrophilic than  $\text{CH}_3^{\text{I}}$ . This implies that it is other energy terms than the initial attraction between reacting groups which govern the substitution process in this case.

The intensities of the  $\text{CH}_3^{\text{I}}$  stretching motions are considerably greater than those of  $\text{CH}_3^{\text{II}}$  but the asymmetric bending vibration 1461  $\text{cm}^{-1}$  of  $\text{CH}_3^{\text{II}}$  is considerably broader and more intense in absorption than 1416, even when allowance is made for a weak absorption at 1444  $\text{cm}^{-1}$  ( $2 \times 723$ ), which is required to account for the profile of the bands. The breadth of the band at 1461 is characteristic, for it is found in the corresponding bands of the methyl esters of aromatic sulphonic acids and is attributed to the overlap of two very close absorptions due to the methyl group having two environments in the *gauche* and *trans*-forms.

The assignment of other frequencies presents more difficulty. The frequency 724  $\text{cm}^{-1}$ , intense in the Raman spectrum and of medium intensity in the infra-red spectrum, has the characteristics to be expected of the C–S vibration. There is a corresponding frequency (750  $\text{cm}^{-1}$ ) in methane sulphonyl chloride and in each of the sulphonic esters, and the variation in frequency corresponds to that expected from the changing substitution (Freeman and Hamby 1957).

There is also evidence that the vibration 814  $\text{cm}^{-1}$  is the S–OMe stretching frequency. All the aromatic sulphonic esters show a vibration  $\sim 790 \text{ cm}^{-1}$  which is not present in the corresponding sulphonyl chlorides. The O–CH<sub>3</sub> frequency in carboxylic esters is ill defined (Bellamy 1954) and we are not able to identify such a stretching frequency in our sulphonic esters.



(b) Aromatic Sulphonic Esters

(i) *SO<sub>2</sub> Stretching Frequencies*.—For these esters a frequency 1182–1193 cm<sup>-1</sup> (mean 1190) is assigned as the symmetric SO<sub>2</sub> stretch rather than 1176, which is also found in similarly substituted, non-sulphonyl, benzene derivatives. The corresponding asymmetric stretch occurs at frequencies 1347–1380 cm<sup>-1</sup> in liquid films, the frequency increasing with electron attracting *p*-substituents or on solution in a non-polar solvent. These characteristic frequencies are similar to those of the corresponding aryl sulphonyl halides and higher than those for methane sulphonyl halides and esters.

(ii) *ortho-Effect*.—Saunders, Murray, and Cleveland (1941) noted the increase in the carbonyl vibration frequencies of acetophenone, benzoyl chloride, and methyl benzoate on substitution of a methyl group in the *ortho*-position. This rise has been interpreted as due to the forcing of the carbonyl group out of the plane of the benzene ring, so reducing its conjugation with the aromatic  $\pi$ -orbitals and increasing its bond order. Aromatic sulphonyl compounds are not expected to show such conjugation in the ground state (Freeman and Hamby 1957) and we find that, whereas the methyl esters of *p*-toluene- and benzene-sulphonic acids have identical asymmetric sulphonyl stretching frequencies, the *o*-toluene sulphonic ester has lower values. As hydrogen bonding also depresses the sulphonyl frequencies it is possible that a weak intramolecular hydrogen bonding occurs between the sulphonyl oxygen and the *o*-methyl group which will be activated by induction.

(iii) *Interaction with Aromatic Frequencies*.—The sulphonic ester group acts in a similar manner to the electronegative halogen substituents in depressing the frequencies of the 1600 and 1490 cm<sup>-1</sup> aromatic bands to lower frequencies; in the *p*-bromo-ester these reach the lower limits of 1578 and 1473 cm<sup>-1</sup>.

It is commonly accepted that certain carbon-hydrogen, out-of-plane, bending vibrations can be used to distinguish *ortho*-, *meta*-, and *para*-disubstituted aromatic molecules from one another. Bellamy (1954) suggests 735–770 cm<sup>-1</sup> and 800–860 cm<sup>-1</sup> as the characteristic regions in which a strong band occurs in the infra-red spectra of the *ortho*- and *para*-derivatives respectively. Ham and Hamby (1953*b*) noted the occurrence of a strong band near 810 cm<sup>-1</sup> in the Raman spectra of *o*-toluene sulphonyl chloride and *o*-toluene sulphonyl fluoride. This was confirmed with a very carefully purified sample of the sulphonyl chloride by Aurnhammer *et al.* (1955), who also showed that a corresponding band of moderate intensity occurred in the same region of the infra-red spectra of *o*-toluene sulphonyl chloride and *o*-toluene sulphonamide. This anomaly seems to be characteristic of *o*-toluene sulphonyl derivatives, for we find a strong band both in scattering and absorption at 810 cm<sup>-1</sup> for methyl *o*-toluene sulphonate. In the *p*-bromobenzene and the *p*-toluene sulphonic esters, the correlation of the bands at 833 and 817 cm<sup>-1</sup> respectively with an out-of-plane C–H bend is reasonable, but with the *p*-nitro-substituted ester there is only a pattern of weak absorptions in this region. Bellamy (*op. cit.*) has noted a similar breakdown of such correlations in dinitro-compounds.

(iv) *The Frequency ~1097 cm<sup>-1</sup>*.—Ham and Hamby (1953*b*) noted that there was a band at about 1080 cm<sup>-1</sup> in the Raman spectra of a series of aromatic

TABLE 3  
VIBRATIONAL SPECTRA OF AROMATIC SULPHONIC ESTERS

Intensity first indicated is that in the Raman spectrum, the second the intensity in the infra-red spectrum. A dash denotes that the band was not observed. Where there was an appreciable difference between the two frequencies we have given the infra-red value which we believe to be the more accurate

Aromatic Sulphonic Esters	Intensity in the Raman and Infra-Red Spectra
Methyl benzene sulphonate (pure liquid)	254 m. —, 316 vs. —, 372 m. —, 463 w. —, 499 w. —, <b>564</b> w. m., <b>588</b> m. vs., 615 s. m., 690 — m., <b>712</b> vs. m., 730 + 737 vw. m., 753 — s., <b>790</b> m. m., 992 vs. s., 1020 m. m., 1039 — m., 1071 — w., <b>1096</b> m. m., 1130 — m., 1176 s. s., <b>1192</b> s. s., 1254 — w., 1292 w. w., 1314 m. w., <b>1339</b> — m., <b>1363</b> w. vs., 1448 w. m., 1480 — m., 1585 s. m., 2844 vw. w., 2891 — vw., 2954 w. m., 3010 vw. w., 3066 s. m., 3014 — vw.
Ethyl benzene sulphonate (pure liquid)	318 m. —, <b>573</b> — m., <b>589</b> vw. vs., 615 m. m., 690 — s., <b>715</b> m. m., 756 — m., 778 w. m., <b>797</b> w. s., 918 — s., 1004 vs. vs., 1025 w. —, 1072 — w., <b>1097</b> m. m., 1163 — m., 1179 s. vs., <b>1190</b> s. vs., 1291 w. w., 1300 — vvw., 1312 s. m., <b>1338</b> — m., <b>1356</b> w. vs., 1369 — s., 1393 — m., 1442 — w., 1449 w. s., 1476 — w., 1481 — m., 1586 s. m., 2872 — vw., 2908 — w., 2940 m. m., 2962 m. vw., 2988 m. m., 3004 — w., 3069 s. m.
Methyl o-toluene sulphonate (pure liquid)	208 m. —, 266 w. —, 298 s. —, 317 w. —, 424 w. —, 479 m. —, 544 s. m., <b>555</b> — m., <b>571</b> w. m., 597 w. vs., 619 — m., 661 w. m., <b>688</b> vs. s., 712 w. m., 764 w. vs., <b>781</b> w. s., <b>811</b> s. vs., 991 w. vs., 1038 + 1067 vs. m., <b>1098</b> w. w., 1139 w. w., <b>1185</b> vs. vs., 1197 w. —, 1285 vw. w., 1296 m. w., 1311 m. w., <b>1337</b> — m., <b>1357</b> w. vs., 1434 — w., 1457 w. m., 1474 — m., 1572 w. w., 1590 — w., 1599 s. m., 2845 — vw., 2895 — vw., 2925 m. vw., 2956 m. m., 3012 — vw., 3066 s. w., 3099 — vw.
Methyl p-toluene sulphonate (pure liquid)	211 m. —, 272 w. —, 288 vs. —, 361 w. —, 388 w. —, 472 w. —, 502 w. —, <b>556</b> w. s., <b>565</b> — m., 634 s. —, <b>661</b> m. m., 688 — vw., 707 w. w., 767 vs. vs., <b>804</b> w. m., 817 m. s., 990 w. s., 1017 — w., <b>1095</b> s. m., 1118 — vw., 1170 vs. vs., <b>1188</b> m. vs., 1212 w. vw., 1292 vw. vw., 1307 m. w., <b>1344</b> — m., <b>1363</b> w. vs., 1400 — vw., 1437 — w., 1456 w. m., 1497 w. m., 1598 vs. m., 2845 — w., 2893 — vw., 2924 s. w., 2954 m. m., 3003 — w., 3030 — w., 3064 v. s. w., 3090 — vw.
Methyl p-bromo-benzene sulphonate*	<b>562</b> — m., 605 w. s., <b>733</b> m. m., 759 — w., <b>789</b> w. vs., 813 — vw., 822 — vw., 833 — m., 957 — w., 982 — vs., 1009 — m., 1068 s. m., <b>1095</b> vw. w., 1115 — vw., 1060 m. m., 1175 s. s., <b>1190</b> m. s., 1215 — vw., 1257 — vw., 1278 — w., 1338 — vw., <b>1358</b> — m., <b>1375</b> — vs., 1392 — m., 1437 — vw., 1457 — w., 1473 — m., 1491 — vw., 1571 — vw., 1578 s. m., 2844 — vw., 2892 — vw., 2955 — w., 3016 — vw., 3065 — w., 3092 — vw.
Methyl p-nitro-benzene sulphonate†	<b>562</b> m., 612 s., 683 m., <b>732</b> m., 747 m., <b>791</b> vs., 814 vw., 841 vw., 858 vw., 866 w., 970 m., 976 s., 1010 w., <b>1096</b> w., 1110 vw., 1178 w., <b>1192</b> s., 1291 vw., 1312 m., 1351 m., <b>1377</b> vs., 1405 m., 1438 vw., 1457 w., 1480 w., 1536 vs., 1609 m., 2842 vw., 2873 vw., 2956 w., 3033 w., 3071 vw., 3105 vw.

\* Raman, incomplete, in  $\text{CHCl}_3$  solution, infra-red "Nujol" mull to  $1200\text{ cm}^{-1}$ , higher frequencies in  $\text{C}_2\text{Cl}_4$  solution.

† Infra-red spectrum only, "Nujol" mull to  $1200\text{ cm}^{-1}$ , higher frequencies in  $\text{CHCl}_3$  solution.

sulphonyl chlorides and about  $1095\text{ cm}^{-1}$  for the corresponding sulphonyl fluorides. Freeman and Hambly (1957) find a frequency in this region for  $\omega$ -styrene sulphonyl chloride. Monosubstituted aromatic compounds do not usually have a vibration in this region except for the halogen derivatives, and in the case of the *p*-chloro- and *p*-bromobenzene sulphonyl halides there are two frequencies in this region.

We now find that in all the aromatic sulphonate esters there is a frequency close to  $1095\text{ cm}^{-1}$  (and two for the *p*-bromo-ester) that is practically independent of the position and nature of another substituent. This frequency falls in the range of C-H in-plane, deformation vibrations, but its nature is obscure, for these vibrations vary with position of substitution while this vibration at  $1095\text{ cm}^{-1}$  varies in intensity but not in frequency. It can be regarded as confirmatory to the conclusion from the  $\text{SO}_2$  stretching bands of the presence of an aromatic sulphonyl derivative. The vibrational spectra of the aromatic sulphonyl esters are summarized in Table 3.

#### IV. ACKNOWLEDGMENTS

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# THERMODYNAMIC DATA FROM GAS-LIQUID PARTITION CHROMATOGRAPHY

By J. R. ANDERSON\* and K. H. NAPIER†

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## Summary

Partition coefficients obtained from gas-liquid partition chromatography have been compared with those obtained in a static system to show that the former are true equilibrium values. The heats and entropies of solution have been obtained from the temperature dependence of the partition coefficients.

## I. INTRODUCTION

Although much work (cf. James and Martin 1952; Phillips 1956) has recently been devoted to gas-liquid partition chromatography (G-LPC) as an analytical tool, there has been little systematic attempt to exploit this technique for thermodynamic data relevant to the solution processes occurring on the column.‡ As recently pointed out by Anderson (1956), the method of presentation of results from G-LPC in terms of a "corrected retention volume" is satisfactory if only the heat of solution is required, but if the entropy of solution is also required the evaluation of the partition coefficient itself is more satisfactory.

For the present paper, the system studied was benzene and cyclohexane with a stationary liquid phase of polyethylene glycol cresyl ether in the temperature range 80–131 °C. The partition coefficients obtained from G-LPC were compared with those obtained in a static system to show that the former were true equilibrium values, and from the temperature dependence of the partition coefficient the heats and entropies of solution were found.

## II. THEORY

As shown previously by Anderson (1956), the partition coefficient  $K$  defined as

$$K = \frac{\text{concentration of solute in stationary liquid phase}}{\text{concentration of solute in gas phase}}$$

(both concentrations in g/ml) is related to the zero-flow retention volume  $v_R^0$  by

$$K = \left( \frac{v_R^0}{\alpha X} - 1 \right) \frac{\alpha}{V} \quad \dots \dots \dots (1)$$

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‡ Since the present paper was prepared a paper by Porter, Deal, and Stross (1956) has appeared in which data from G-LPC are correlated in a systematic way with solution thermodynamics.

where  $\alpha$  = gas space volume fraction of the column,

$\gamma$  = stationary liquid phase volume fraction of the column,

$X$  = total volume of the column.

### III. EXPERIMENTAL

The equipment for G-LPC was similar to that described previously by Anderson and Napier (1956) based on the design of Ray (1954). The internal diameter of the column was 4 mm. The benzene and cyclohexane were analytical reagent purity. The polyethylene glycol cresyl ether was a commercial sample supplied by Messrs. Robert Bryce Ltd., Sydney. It was supported in the column either on alumina (cf. Anderson and Napier 1956) or on kieselguhr similar to that described by James and Martin (1952). Rate of flow of carrier gas (dry nitrogen) was measured approximately with an all-glass rotameter and accurately with a moving bubble flowmeter. To give a flow rate of 25 ml/min the column with the alumina packing required a pressure drop of approximately 12 cm Hg, while the columns packed with kieselguhr required approximately 60 cm Hg. Retention times were measured from the distances on the recorder chart, the speed of which was carefully calibrated. The sample size was standardized at 0.01 ml of liquid. To obtain the true retention volumes, corrections were made for the dead space in the gauge and connecting tubes.

The apparatus used for static measurement of the partition coefficient consisted of a known amount of polyethylene glycol cresyl ether contained in a vessel which was connected to a second vessel containing benzene (or cyclohexane) vapour at known pressure by a breakable glass seal. On breaking the seal, using a magnetic stirrer equilibrium was reached, when the pressure was again read. The apparatus was constructed entirely of glass, completely immersed in a thermostat. Pressures were read on a mercury manometer which was also thermostated.

#### (a) Evaluation of Column Variables

The total column volume  $X$  was determined by filling the empty column with mercury and weighing the liquid. The stationary liquid phase volume fraction  $\gamma$  was computed from the density of the liquid at column temperature and its total weight in the column, which was determined by analysis of the packing after use.

The gas-space volume fraction  $\alpha$  was determined by three methods: (i) from the retention volume of a sample of inert gas such as hydrogen or helium; (ii) from the theory of gas flow through a porous plug; (iii) from the difference between the total column volume and the volume of the liquid and solid phases. Because of the uncertainty in estimating the effective volume of the solid phase, method (iii) served mainly as a check. Method (i) assumes that the "inert" gas is not sorbed by any of the column packing and this is confirmed since the values of  $\alpha$  so found were almost independent of temperature in the range 20–131 °C (being only influenced by the thermal expansion of column components) and were the same for helium and hydrogen. Method (ii) which was limited

to the alumina support used the equation of Carmen (1950), and also served mainly as a check:

$$\frac{GL\eta}{A} / p = \frac{\alpha^3}{5 \cdot 0 S^2 (1 - \alpha)^2}, \quad \dots \dots \dots (2)$$

where  $L$  = length of column (cm),

$A$  = cross-section area of column (cm<sup>2</sup>),

$\eta$  = viscosity of gas flowing (poise),

$S$  = specific surface of packing (cm<sup>2</sup>/ml) of column,

$p = \frac{1}{2}(p_1 + p_2)$ , where  $p_1$  and  $p_2$  are the entrance and exit pressures respectively (dyn/cm<sup>2</sup>),

$G = p_1/(p_1 - p_2)t$ , where  $t$  is the time in sec for 1 ml of gas to flow at pressure  $p$ .

From the slope of the straight line obtained by plotting  $GL\eta/A$  against  $p$  the value of the right-hand side of (2) was found. Substituting  $1 - \alpha = 4/3\pi r^3 N$  and  $S = 4\pi r^2 N$ , where  $r$  is the mean particle radius (assumed spherical) and  $N$  is the mean number of particles per ml of packing,  $r$  was computed;  $N$  ( $2 \cdot 06 \times 10^4$  particles/ml) being obtained by direct counting. This method yielded  $r = 0 \cdot 0185$  cm and  $\alpha = 0 \cdot 46$ . For the same alumina packing, method (i) gave  $\alpha = 0 \cdot 39$  and method (iii)  $0 \cdot 37$ . The careful estimation of  $\alpha$  is of some importance since errors here will contribute to the ultimate accuracy with which thermodynamic data may be obtained.

#### IV. RESULTS

##### (a) Variation of Retention Volume with Pressure Drop

James and Martin (1952) have shown that if the carrier gas obeys the laws of viscous flow and if the solution process is always at equilibrium the retention volume is given by

$$v_R = \frac{2}{3} v_R^0 \times f(p_1/p_2), \quad \dots \dots \dots (3)$$

where

$$f(p_1/p_2) = \frac{(p_1/p_2)^3 - 1}{(p_1/p_2)^2 - 1}.$$

If equation (3) is obeyed, a plot of  $v_R$  against  $f(p_1/p_2)$  should give a straight line with a slope equal to  $\frac{3}{2} v_R^0$  and an intercept (when  $p_1/p_2 = 1$ ) of  $v_R^0$ . It was found that a plot of  $v_R$  against  $f(p_1/p_2)$  always gave a straight line, but the slope frequently tended to fall slightly below the theoretical value. Because of this  $v_R^0$  was always obtained by extrapolation. Significant error may result if equation (3) is used to evaluate  $v_R^0$  from a single experimental point, as was done by Littlewood, Philips, and Price (1955).

##### (b) Partition Coefficients at Low Hydrocarbon Concentration

Three columns of widely differing parameters were used. They are summarized in Table 1. Values of  $\alpha$  are given as independent of temperature because of the comparatively large uncertainty in the estimation of this quantity ( $\pm 5$  per cent.). The uncertainty in each value of  $\gamma$  is about  $\pm 1$  per cent. From the values of  $v_R^0$  and column parameters the partition coefficients were

TABLE I  
 DESCRIPTION OF VARIOUS COLUMNS

	$\alpha$	$X$ (ml)	$\gamma$		
			80 °C	100 °C	131 °C
Column 1 Alumina support ..	0.39	38.0	0.309	0.314	0.320
Column 2 Kieselguhr support	0.72	19.2	0.182	0.184	0.189
Column 3 Kieselguhr support	0.68	19.2	0.232	0.236	0.241

calculated using equation (1) and the results are summarized in Table 2. The retention volumes and partition coefficients remained unaffected by increasing or decreasing the sample size by a factor of two.

 TABLE 2  
 RETENTION VOLUMES AND PARTITION COEFFICIENTS AT VARIOUS TEMPERATURES

	$v_R^0$ (ml)			$K$		
	80 °C	100 °C	131 °C	80 °C	100 °C	131 °C
Column 1 $\begin{cases} C_6H_6 \\ C_6H_{12} \end{cases}$	878	512	304	73.6	41.7	23.8
	238	172	126	19.1	13.2	9.1
Column 2 $\begin{cases} C_6H_6 \\ C_6H_{12} \end{cases}$	245	165	85	66.1	42.8	19.6
	81	59	46	19.2	12.8	8.8
Column 3 $\begin{cases} C_6H_6 \\ C_6H_{12} \end{cases}$	348	220	138	75.0	45.6	26.9
	95	79	60	18.4	14.5	10.1

A comparison of the mean partition coefficients obtained by G-LPC and by the static method is given in Table 3. Measurements were made in the static system with a solute concentration of about 1 per cent. (w/w) which was estimated to be about a factor of two greater than the maximum concentration likely in a solute band in the column.

 TABLE 3  
 MEAN PARTITION COEFFICIENTS FROM G-LPC AND STATIC MEASUREMENT

				80 °C	100 °C	131 °C
G-LPC $\begin{cases} C_6H_6 \\ C_6H_{12} \end{cases}$	..	..	..	71.6	43.4	23.4
	..	..	..	18.9	13.5	9.3
Static method $\begin{cases} C_6H_6 \\ C_6H_{12} \end{cases}$	..	..	..	73.0	44.1	20.1
	..	..	..	19.9	15.0	7.8

(c) Partition Coefficients at Higher Hydrocarbon Concentrations

To study the possible dependence of the partition coefficient on concentration, benzene vapour was introduced at constant partial pressure into the

carrier gas thus equilibrating the column with benzene of known concentration before introducing the hydrocarbon samples in the usual way. The partial pressure of benzene in the gas stream was 90 mm Hg at the entrance to the column and the retention volume of both benzene and *cyclohexane* were unchanged from the values in Table 2. An equilibrium partial pressure of benzene in excess of 90 mm Hg could not be used in the present apparatus because of condensation of benzene in the hot-wire gauge.

#### (d) Peak Shape

With the size of sample used the peaks were not quite symmetrical in shape, showing a slight tendency for tailing. Within experimental error, this departure from symmetry was independent of flow rate in the range 5–25 ml/min.

### V. DISCUSSION

The constancy of retention volumes with changing sample size and changing benzene concentration shows that in this region the solutes obey Henry's law. The departure of peak shape from strict symmetry was probably caused by small non-uniformity in the concentration of the sample as it entered the column.\*

The partition coefficients obtained by G-LPC and static measurement are generally in good agreement and confirm the validity of the chromatographic procedure for their evaluation.

TABLE 4  
CALCULATED THERMODYNAMIC QUANTITIES

			$\Delta H$ (kcal/mole)	$\Delta S$ (e.u.)
Benzene				
80 °C	}	.. ..	-7.4 <sub>8</sub>	-13.2
100 °C				
131 °C				
<i>cyclo</i> Hexane				
80 °C	}	.. ..	-5.2 <sub>8</sub>	- 9.5
100 °C				
131 °C				

The heat of solution of the hydrocarbon vapour,  $\Delta H$ , may be obtained from the relation

$$\frac{\partial (\log_e K_B)}{\partial (1/T)} = -\frac{\Delta H}{R},$$

in which  $K_B$  is Bunsen's distribution coefficient defined by

$$K_B = 273K/T$$

\* This effect has since been discussed quantitatively by Porter, Deal, and Stross (1956).



where  $T$  is the absolute temperature. Since the free energy of solution  $\Delta G$  is given by

$$\Delta G = -RT \log_e K_B,$$

the entropy of solution of the vapour may be computed from

$$\Delta S = (\Delta H - \Delta G)/T,$$

and the calculated values are given in Table 4.

The greater values of  $K$  for benzene are clearly due to numerically greater  $\Delta H$  and  $\Delta S$  terms. This treatment makes it clear that if  $\Delta H$  and  $\Delta S$  are known for a particular system, its behaviour in G-LPC may be predicted.

This method of measurement of solution thermodynamics should be useful for the study of three component mixtures.

#### VI. ACKNOWLEDGMENT

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# ELECTROSTATIC, POLAR, AND STERIC FACTORS IN THE ACID HYDROLYSIS OF THE DIPEPTIDES

By R. J. L. MARTIN\*

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## Summary

Published kinetic data concerning the rates of hydrolysis of dipeptides are discussed and interpreted in terms of the expected electrostatic, polar, and steric influences of the constituent groups. The evidence is consistent with a reaction mechanism in which a proton is first added reversibly to the peptide nitrogen, and the amide cation so formed reacts at the carbonyl carbon atom with a water molecule in a rate-controlling bimolecular substitution.

Substitution at the *glycyl* carbon atom of the parent substance glycylglycine will alter the steric hindrance to substitution by the water molecule. On the other hand, the polar effect of these substituents will be small and will have little influence on the rate of reaction.

Substituents at the *glycine* carbon atom introduce polar factors only with little evidence of steric effects. This absence of a steric effect applies both to the formation of the amide cation and to the substitution by the water. Electron repelling groups decrease the rate of hydrolysis and must be considered to have a greater effect on decreasing the electron accession to the peptide nitrogen necessary for the rupture of the bond than on increasing the concentration of the amide cation. Electron attracting substituents act in the reverse manner.

There is some evidence for a small amount of steric compression between groups on either side of the peptide bond for the bimolecular reaction with water.

## I. INTRODUCTION

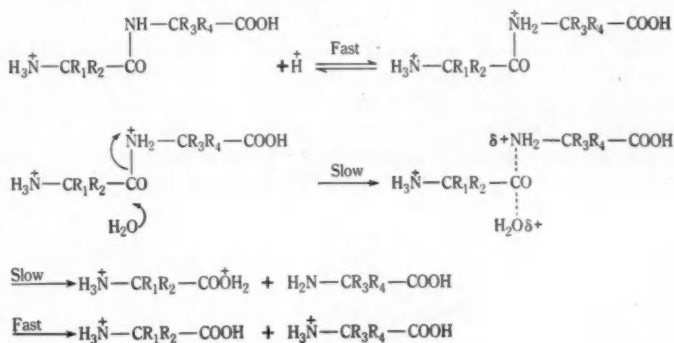
Acid hydrolysis has been used extensively for determining the amino-acid residues in a polypeptide chain, and the ease with which a peptide bond breaks is determined by the various electrostatic, polar, and steric factors involved in the reaction (see review by Leach 1953). Kinetic investigations with model dipeptides have been undertaken by several workers to determine the influence of each factor on the reaction rate.

Synge (1945) and Harris, Cole, and Pon (1956) found the rate of hydrolysis to be first order with respect to the dipeptide concentration for a large excess of acid. Lawrence and Moore (1951) and Martin (1955) for smaller concentrations of acid found the reaction to be first order with respect to both the dipeptide and hydrogen ion concentrations. Synge (1945) found that the decrease in rate caused by substituents on either side of the peptide bond depended upon the size and position of branching in the chain and concluded that these groups sterically hindered the access of hydrogen ions to the peptide bond. Synge

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also noticed that substitution at the glycyl carbon atom reduced the rate more than the same substituents at the glycine carbon atom. Lawrence and Moore (1951) found that substituents on either side of the peptide bond caused changes in either the energy or entropy of activation and attempted to explain these effects in terms of polar factors. Apart from the steric factors, Synge (1945), Sanger (1952), and Harris, Cole, and Pon (1956) agree that the positively charged terminal amino group will reduce the rate by repelling the approach of hydrogen ions. Lawrence and Moore (1951) have shown that this positive charge increases the entropy of activation and has little effect on the energy of activation.

Gordon, Martin, and Synge (1941) also recognized that factors other than steric and electrostatic must be operating because it was found that peptide bonds involving the amino groups of serine and threonine are split very readily. Harris, Cole, and Pon (1956) have shown that the *C*-terminal serine and aspartic acid dipeptides have faster rates and that *N*-terminal serine and aspartic acid



Mechanism 1

dipeptides have slower rates of hydrolysis than the corresponding glycine dipeptides. Elliott (1949, 1950, 1952) has shown that acids catalyse the *N*-acyl to *O*-acyl migration for serine and threonine so that the peptide bond is converted to an ester linkage. Desnuelle and Bonjour (1952) found that *N*-acetylamino alcohols and *N*-acetylamino acids were hydrolysed faster than the corresponding *N*-acetylaminos.

Synge (1945), Sanger (1952), and Harris, Cole, and Pon (1956) consider the mechanism to be a reaction between the oxonium ion and the dipeptide. Lawrence and Moore (1951) suggest that the oxonium ion is hydrogen bonded with the peptide cation in the activated complex.

For an almost identical reaction, the acid hydrolysis of the amides, Benrath (1926) and Euler and Ölander (1928) have concluded that it is the amide cation which reacts with a water molecule. Ingold (1953, p. 784) has suggested that the rate-controlling step is a bimolecular substitution by a water molecule at the carbonyl carbon atom of the amide cation and has discussed the effect of substituents on the reaction rate. Bunton, Lewis, and Llewellyn (1954) and

Bender and Ginger (1955) have confirmed this mechanism for benzamide, and have shown by isotopic oxygen exchange that the proton is added to the nitrogen and not the carbonyl oxygen.

For the hydrolysis of glycylglycine in aqueous acetic acid, Martin (1955) has suggested that the mechanism of the reaction is identical with that for the amides. In this mechanism there is an initial fast reversible addition of a proton to the peptide nitrogen and the amide cation so formed reacts at the carbonyl carbon atom with a water molecule. This bimolecular substitution is the rate-controlling step of the reaction.

This discussion is intended to consider the effect of the various electrostatic, polar, and steric factors on the reaction rate. Briefly, it is shown that the mechanism of the reaction is that given by mechanism 1, that substitution at the glycine carbon atom will only alter the polar effects and that substitution at the glycyl carbon atom will only change the steric effects.

## II. THE MECHANISM OF THE REACTION

There are two possible mechanisms to consider for the reaction and one of these, mechanism 1, has already been explained. The configuration for the transition state of this mechanism is given in Figure 1 and resembles that given by Ingold (1953, p. 784) for the acid hydrolysis of the amides. In order that the incoming and outgoing groups shall interfere with one another as little as possible they are situated on opposite sides of the transition complex as in Figure 1.

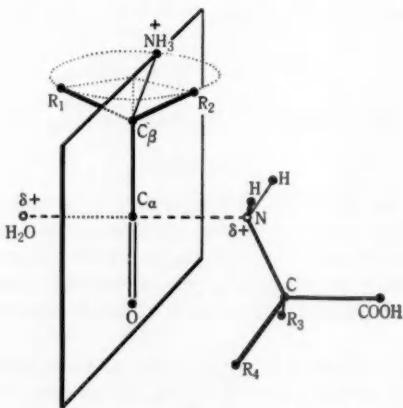


Fig. 1

In this model the nuclei of the substituting O atom (water molecule), the  $C_\alpha$  (carbonyl) carbon atom at which the substitution takes place, and the displaced N atom are collinearly arranged and lie in the plane of the paper. During the reaction the distances between the  $C_\alpha$  and N atoms will change from that of a covalent bond to that of complete separation. The latter distance is the sum of the van der Waals radii. In the transition state, the length of the partial

bond will have an intermediate value which approximates to the sum of the covalent radius of carbon and the mean of the covalent and van der Waals radii of nitrogen. The length of the  $O-C_\alpha$  partial bond can be calculated in a similar manner. The nuclei of the  $C_\alpha$ ,  $C_\beta$ , and carbonyl O atoms will lie in a plane perpendicular to the line  $OC_\alpha N$ . Free rotation about the bond  $C_\alpha-C_\beta$  will allow the groups  $R_1$ ,  $R_2$ , and  $NH_3^+$  to take up positions so that the steric interference with the incoming and outgoing groups and the repulsive forces are a minimum. All other bond lengths and angles apart from those just defined are assumed to have the normal covalent values.

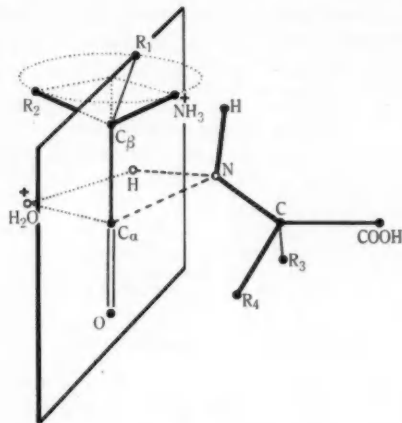
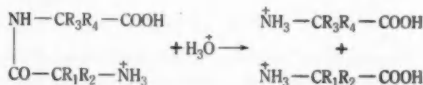


Fig. 2

The other mechanism suggested by the discussions of Syngé (1945), Sanger (1952), and Harris, Cole, and Pon (1956) involves a direct attack by the oxonium ion on the peptide and is based on the equation for the overall reaction for the hydrolysis. The possible transition state for this reaction is given in Figure 2. In order to facilitate the formation of the partial bond between H and N it will be necessary for the partial bonds  $O-C_\alpha$  and  $C_\alpha-N$  to form an angle much less than  $180^\circ$  at the  $C_\alpha$  atom



Mechanism 2

For mechanism 1, if the concentration of the amide cation is assumed small and proportional to  $[H^+][\text{dipeptide HX}]$  the rate of hydrolysis is proportional to  $[H_2O][H^+][\text{dipeptide HX}]$ .

Similarly for mechanism 2 the rate of hydrolysis is proportional to  $[H_3O^+][\text{dipeptide HX}]$ .

In all the kinetic data reported, the concentration of water is large and will remain constant during reaction. For both mechanisms, therefore, the rate of hydrolysis is first order with respect to the hydrogen ion and dipeptide concentrations and it is impossible to choose between the mechanisms by determining the order of the reaction. There are however important differences between the two transition states suggested which allow a choice to be made.

For a transition state with the configuration given in Figure 2 the repulsive force between the oxonium ion and the terminal amino group occurs during formation of the transition state and should therefore be manifested by an increase in the activation energy. This repulsive force will also reduce the number of collisions between the reactants and will produce in addition a large decrease in the frequency factor.

TABLE 1  
THE EFFECT OF A POSITIVELY CHARGED GROUP ON THE REACTION RATE  
AND THE ARRHENIUS PARAMETERS  
Arrhenius parameters calculated from the data of Lawrence and  
Moore (1951)

Dipeptide	Relative Rate at 70 °C	<i>E</i> (cal)	Log <sub>10</sub> <i>B</i> *
Acetyl glycine ..	10.1	21	9.3
Glycyl glycine ..	1.0	20	7.5

\* *E*, activation energy; *B*, frequency factor.

For mechanism 1, on the other hand, this repulsive force between the proton and the positive terminal amino group occurs during the formation of the amide cation, thereby reducing its concentration so that it will cause changes principally in the Arrhenius frequency factor or entropy of activation. The reaction between water and the amide cation however does lead to the formation of partial positive charges in the transition state but the repulsive force between these will be less than that for mechanism 2.

The results given in Table 1 show that the positively charged terminal amino group in glycylglycine reduces the rate of hydrolysis as compared with acetyl glycine which contains no such positive charge. It will also be noted that the positive charge produces a large decrease in the frequency factor and a small decrease rather than an increase in the activation energy. The experimental evidence would therefore appear to support mechanism 1.\*

\* This comparison between acetyl glycine and glycylglycine may appear to be a doubtful procedure because these compounds differ both with respect to their steric configuration and to the inductive effects of their substituent groups. The magnitude of the changes in rate and Arrhenius parameters produced by these differences in steric and inductive effects is small compared with the changes produced by the electrostatic effect of the  $\text{NH}_3^+$  group on the concentration of the amide cation.

Glycylglycine is a mono- $\beta$ -substituted derivative of acetyl glycine and later discussion will show that these mono- $\beta$ -substituents produce a small amount of steric hindrance with small changes in reaction rate and activation energy. The inductive effect of  $\beta$ -substituents has little effect on the rate of a bimolecular reaction.

The rate of hydrolysis of a homogeneous polypeptide chain increases with the number of peptide bonds present (Leach 1953, p. 42). As the chain length increases, the electrostatic effect between the terminal amino group and the peptide bond furthest away will decrease. This will bring about an increase in both the amide cation concentration and the reaction rate. In conformity with mechanism 1, Lawrence and Moore (1951) have shown that the increase in rate of hydrolysis of diglycylglycine as compared with that of glycylglycine is accompanied by changes in the entropy of activation.

The results obtained by Martin (1955) for the hydrolysis of glycylglycine in acetic acid containing small amounts of water support mechanism 1. Noyce and Castelfranco (1951) and Smith and Elliot (1953) have shown that the acidity functions of strong acids in acetic acid decrease with an increasing water concentration; in other words, an increasing water concentration increases the solvation of the hydrogen ions.

TABLE 2  
SECOND-ORDER VELOCITY CONSTANTS FOR THE HYDROLYSIS OF GLYCYL-  
GLYCINE IN AQUEOUS ACETIC ACID (MARTIN 1955)

Water (% by vol)	$k_2 \times 10^4$ ( $\text{sec}^{-1} \text{ g-mol}^{-1} \text{ l}$ )	
	100 °C	120 °C
0.25	—	4.86
0.50	1.33	5.46
1.0	1.55	6.06
2.0	1.50	6.36
5.0	1.26	5.42

Under these circumstances mechanism 2 would require the velocity constant to increase with the water concentration. On the other hand, the increase in rate for mechanism 1, caused by the increase in the water concentration, is counteracted by the reduction in rate, caused by the decrease in the hydrogen ion activity and the amide cation concentration, so that the observed rates, given in Table 2, are almost independent of the water concentration.

### III. SUBSTITUTION AT THE GLYCYL CARBON ATOM

The introduction of the groups  $R_1$  and  $R_2$  at the glycyl carbon atom should produce similar effects on the reaction rate to those of  $\beta$ -substituents for other bimolecular nucleophilic substitutions. Dostrovsky, Hughes, and Ingold (1946) have shown that the large decrease in rate for the bimolecular reactions of the alkyl halides, which is brought about by increasing  $\beta$ -methylation, is due to an increase in the steric hindrance to a bimolecular reaction. On the other hand, the polar effects of the  $\beta$ -methyl groups were considered to be small and to have no influence on the reaction rate.

Mechanism 1 for the acid hydrolysis of the dipeptides is identical with Ingold's (1953, p. 767) mechanism  $A_{AC}2$  (bimolecular acid hydrolysis with acyl-

oxygen fission) for the acid hydrolysis of the esters. From the examination of a large amount of experimental data, Ingold (1953, p. 767) has shown that substituents at the  $\beta$ -carbon atom, irrespective of whether they are electron attracting or repelling, do not exert polar effects on the rate of hydrolysis of the esters. There is however an overall decrease in rate for increasing substitution at the  $\beta$ -carbon atom because of an increase in the steric hindrance.

TABLE 3  
RELATIVE RATES FOR THE ACID HYDROLYSIS OF THE DIPEPTIDES  
Effect of substitution at the glycyl carbon atom

Class	Dipeptide	Synge (1945)	Lawrence and Moore (1951)			Harris, Cole, and Pon (1956)
				<i>E</i> (cal)	$\text{Log}_{10} B$	
1	Glycylglycine .. ..	1.00	1.00	20	7.5	1.00
	DL-Alanylglycine .. ..	0.62	0.56	21	7.7	0.69
	L-Serylglycine .. ..					0.40
	L-Leucylglycine .. ..		0.18	22	7.8	0.20
	DL-Leucylglycine .. ..	0.23				
	Valylglycine .. ..	0.015				
2	L-Seryl-L-alanine .. ..					0.74*
	Glycyl-L-alanine .. ..					0.37
	Glycyl-D-alanine .. ..					0.40
	Glycyl-DL-alanine .. ..	0.62				
3	Glycyl-L-leucine .. ..		0.48			0.34
	Glycyl-DL-leucine .. ..	0.40				
	Alanyl-leucine .. ..					0.31
	L-Leucyl-D-leucine .. ..					0.057
	DL-Leucyl-DL-leucine .. ..	0.048				
4	Glycyl-DL-tryptophan .. ..	0.35				
	Glycyl-L-tryptophan .. ..		0.44			
	L-Leucyl-L-tryptophan .. ..	0.041				
5	Glycyl-L-aspartic acid .. ..					1.94
	L-Leucyl-L-aspartic acid .. ..					0.86
6	Glycyl-L-serine .. ..					1.83
	L-Alanyl-L-serine .. ..					1.14
	L-Seryl-L-serine .. ..					0.40

\* The value obtained for the rate of hydrolysis of L-seryl-L-alanine is an approximate value which does not fit in with the relative rate sequences obtained for other seryl dipeptides.

Ingold (1953, p. 784) also considers that substitution at the  $\beta$ -carbon atom in the amides will produce not only a negligible polar effect but a decrease in rate due to steric hindrance. By analogy, substituents  $R_1$  and  $R_2$  at the glycyl carbon atom would be expected to hinder the rate of hydrolysis of the dipeptides sterically and to have a negligible polar effect on the reaction rate.



Unfortunately, the kinetic studies on the acid hydrolysis of the dipeptides are very scanty. The few results that are available have been arranged in Table 3 into classes with the same substituents  $R_3$  and  $R_4$  at the glycine carbon atom so that it would be possible to determine the effect of substituents  $R_1$  and  $R_2$  at the glycyI carbon atom on the reaction rate. Information is available only for  $R_1 = \text{H}$  and  $R_2 = \text{CH}_3$ ,  $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ,  $\text{CH}(\text{CH}_3)_2$ , and  $\text{CH}_2\text{OH}$ . Except for valylglycine the change in rate within each class is small and at the most eight-fold. The relative rate sequence decreases in the order  $R_2 = \text{H} > \text{CH}_3 > \text{CH}_2\text{OH} > \text{CH}_2\text{CH}(\text{CH}_3)_2 > \text{CH}(\text{CH}_3)_2$ .

In this series of substituents,  $\text{CH}_2\text{OH}$  is electron attracting while the others are electron repelling and the relative rate sequence is therefore not dependent upon the polar influence of these groups. The decrease in the relative rate is in the order of increasing size of the group  $R_2$  indicating that the relative rate sequence can be considered due entirely to a steric retardation. The branching of the chain in valine occurs closer to the peptide bond than the branching of the leucine chain and the steric hindrance for valine will be greater than that for leucine, so that there is a greater decrease in rate for valylglycine than for leucylglycine. Of the few results available for the Arrhenius parameters there is a small increase in the activation energy as required for an increase in the steric hindrance and very small changes in the frequency factor.

#### IV. SUBSTITUTION AT THE GLYCINE CARBON ATOM

The substituents  $R_3$  and  $R_4$  at the glycine carbon atom can, if they exert any steric effects, hinder either the formation of the amide cation, or the reaction between water and the amide cation.

A steric effect which decreases the concentration of the amide cation will increase its acidity. Ingold (1953, p. 743) distinguishes two steric factors which can alter the acidity, a primary steric effect which operates in different degrees for the conjugate acid and base, and a secondary steric effect, in which twisting of the acidic or basic group causes a breakdown in conjugation and an alteration in the mesomeric effect on acidity. In the case of dipeptides the conjugate acid with its positive charge will have a larger solvation shell than the conjugate base, and steric compression if present will therefore tend to reduce the concentration of the amide cation. The reduction in the rate of hydrolysis caused by this primary steric effect, if present, would be dependent upon the size of the substituent. Since the conjugated system associated with the peptide bond is confined to three atoms which will always remain planar irrespective of the amount of twisting, there is no possibility of a breakdown in conjugation and the operation of the secondary steric effect.

The *N*-butylacetamides have similar steric configurations to the peptides in the vicinity of the nitrogen atom. The acidity constants of their conjugate acids have been determined by Goldfarb, Mele, and Gutstein (1955) and are given in Table 4. The electron repelling effects of methyl groups will tend to decrease the acidity of the amide conjugate acid and therefore the polar and steric effects, if present, of increasing methyl substitution will tend to oppose one another in affecting the acidity.

The results show that with increasing methyl substitution at the carbon atom adjacent to the nitrogen in the *N*-butylacetamides there is a slight increase in acidity followed by a larger decrease.

The decrease in acidity can be attributed to the stronger electron repelling effect of the *tert*.-butyl group. It is usually found that when sufficient groups have been added to a molecule for steric effects to appear, the further introduction of groups at the same atom causes an increase in the steric effect greater than that corresponding with linearity. Therefore, it would be expected that if steric effects were operating, *N*-*tert*.-butylacetamide would show a larger increase in acidity than *N*-*sec*.-butylacetamide. We can only conclude that steric

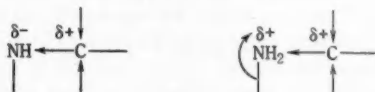
TABLE 4  
ACIDITY CONSTANTS FOR *N*-BUTYLACETAMIDES (GOLDFARB, MELE, AND GUTSTEIN 1955)

Alkyl group	<i>n</i> -Butyl	<i>sec</i> .-Butyl	<i>tert</i> .-Butyl	<i>iso</i> Butyl
Acidity constant (mole l <sup>-1</sup> )	0.71	0.79	0.48	0.98

factors, if they are operating at all, play only a secondary role to the polar factors in affecting the acidity of the conjugate acids of the *N*-butylacetamides. Similarly, as discussion below will indicate, there appear to be no steric factors operating for substituents  $R_3$  and  $R_4$  at the glycine atom in the formation of the amide cation from the dipeptide.

With regard to the steric hindrance to substitution by a water molecule at the carbonyl-carbon atom, the groups  $R_3$  and  $R_4$  at the glycine carbon atom are part of the outgoing group and reference to Figure 1 will show that there should be ample room for this group to arrange itself by rotation about the various bonds and bring steric hindrances to a minimum. No steric hindrance therefore is expected from the groups  $R_3$  and  $R_4$  at the glycine carbon atom unless they are excessively bulky.

Although the substituents  $R_3$  and  $R_4$  at the glycine carbon atom are not expected to exhibit much steric hindrance, they do however exert two opposing polar effects on the reaction rate. If the groups  $R_3$  and  $R_4$  are electron repelling, the basicity of the peptide nitrogen and the concentration of the amide cation will be increased so that there will be a tendency to increase the rate of reaction.



The continued operation of this polar effect after the formation of the amide cation will tend to reduce the rate of reaction by decreasing the electron transfer to the peptide nitrogen necessary for the rupture of the bond. Similarly, electron attracting groups will tend to reduce the concentration of the amide cation and increase the electron accession to the peptide nitrogen.

The results available for the hydrolysis of the dipeptides have been arranged in Table 5 so that substituents  $R_1$  and  $R_2$  at the glycyI carbon atom are the same for the compounds within each class. An examination of Table 5 shows that

steric factors, if they are present, play a secondary role to the polar factors. For example, the  $\text{CH}_2\text{CH}(\text{CH}_3)_2$  group of leucine and the  $\text{CH}_2\text{COOH}$  group of aspartic acid have approximately the same size but the dipeptides *X*-leucine

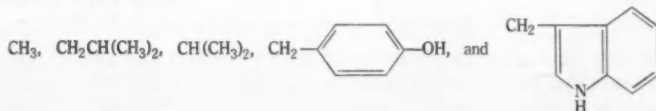
TABLE 5  
RELATIVE RATES FOR THE ACID HYDROLYSIS OF THE DIPEPTIDES  
Effect of substitution at the glycine carbon atom

Class	Dipeptide	Synge (1945)	Lawrence and Moore (1951)	Harris, Cole, and Pon (1956)
1	Glycyl-L-aspartic acid ..			1.94
	Glycyl-L-serine .. ..			1.83
	Glycylglycine .. ..	1.00	1.00	1.00
	Glycyl-D-alanine .. ..			0.40
	Glycyl-L-alanine .. ..			0.37
	Glycyl-DL-alanine .. ..	0.62		
	Glycyl-L-leucine .. ..		0.48	0.34
	Glycyl-DL-leucine .. ..	0.40		
	Glycyl-L-tyrosine .. ..		0.52	0.43
	Glycyl-L-tryptophan ..		0.44	
	Glycyl-DL-tryptophan ..	0.35		
	Glycyl-DL-valine .. ..	0.31		
2	L-Alanyl-L-serine .. ..			1.14
	DL-Alanylglycine .. ..	0.62	0.56	0.69
	Alanyl-leucine .. ..			0.31
3	L-Leucyl-L-aspartic acid ..			0.86
	L-Leucylglycine .. ..		0.18	0.20
	DL-Leucylglycine .. ..	0.23		
	L-Leucyl-L-glutamic acid ..			0.23
	L-Leucyl-D-leucine .. ..			0.057
	DL-Leucyl-DL-leucine .. ..	0.048		
	L-Leucyl-L-tryptophan ..	0.041		
	L-Seryl-L-alanine .. ..			0.74*
	L-Seryl-L-serine .. ..			0.40
	L-Serylglycine .. ..			0.40

\* Approximate value.

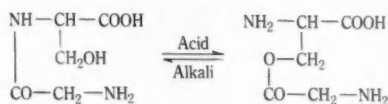
and *X*-aspartic acid react slower and faster respectively than *X*-glycine, indicating that the rate is governed by the polar effects of substituents. *X* represents a common amino acid residue for the series of compounds under discussion.

The dipeptides *X*-alanine, *X*-leucine, *X*-valine, *X*-tyrosine, and *X*-tryptophan all react at approximately the same but slower rate than *X*-glycine. Their substituent groups



differ much in size and therefore no obvious steric retardation is evident. The small differences in rate of these various dipeptides can be explained by differences in the polar factors of these groups. Because these groups are all electron repelling and cause a decrease in rate, they have a greater effect on reducing the rate at which the peptide bond breaks than on increasing the concentration of the amide cation.

The  $\text{CH}_2\text{OH}$  and  $\text{CH}_2\text{COOH}$  groups which are electron attracting cause the dipeptides *X*-serine and *X*-aspartic acid to react faster than *X*-glycine. This faster rate of hydrolysis for the *X*-serine dipeptides is due to the *N*-acyl to *O*-acyl migration which Elliott (1949, 1950, 1952) has shown to occur with acid, and this example is more strictly one of ester hydrolysis.



Desnuelle and Bonjour (1952) found that *N*-acetylamino acids on account of the free carboxyl groups present hydrolysed at faster rates than the corresponding *N*-acetylaminos. A further increase in rate was obtained by these workers with the introduction of a second free carboxyl group. These results therefore agree with those for *X*-aspartic acid dipeptides and show that electron attracting groups such as the carboxyl increase the rate of hydrolysis. If the carboxyl group had a simple polar effect on the rupture of the amide bond then this polar effect would decrease as the distance of this group from the nitrogen increased. Desnuelle and Bonjour (1952) find that the rate decreases in the order  $\beta\text{-COOH} > \alpha\text{-COOH} > \gamma\text{-COOH}$ . This immediately suggests that the faster rates of hydrolysis of the  $\beta$ -carboxyl compounds may be due to factors other than polar effects such as isomerization or cyclization.

It may be thought that the  $\text{CH}_2\text{---}\langle\text{benzene ring}\rangle\text{---OH}$  group of tyrosine would

be electron attracting because the inductive effect of the hydroxyl group would be relayed through the conjugated system. However, the more powerful mesomeric effect of the hydroxyl group when coupled with a conjugated system

would make the  $\text{CH}_2\text{---}\langle\text{benzene ring}\rangle\text{---OH}$  group electron repelling.

It is interesting to compare the results for valylglycine and glycylvaline, where in the former there is a large decrease in rate relative to glycylglycine arising from a steric hindrance, while in the latter, where a polar factor only is operating, there is a much smaller decrease in rate relative to glycylglycine.

It should be possible to determine whether there is any steric compression between substituents on either side of the peptide bond by comparing the decrease in relative rates between the various classes in Table 5. This is rather

difficult because the different workers obtain small differences in rate for particular dipeptides relative to glycylglycine. In class 1 the rates of hydrolysis of glycyl-leucine and glycyltryptophan relative to glycylglycine are 0.37 (Synge), 0.46 (Lawrence and Moore), and 0.34 (Harris, Cole, and Pon). Leucyl-leucine and leucyltryptophan in class 3 have rates relative to leucylglycine of 0.19 (Synge) and 0.29 (Harris, Cole, and Pon). Synge's results therefore indicate a small but definite steric compression while the results of Harris, Cole, and Pon indicate a small almost negligible steric compression. At the moment it can only be concluded that the steric compression between the groups on either side of the peptide bond is small in the few cases considered, but it would be expected to be much stronger in those cases where there are bulky substituents on either side of the bond.

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# THE KINETICS OF THE ACID HYDROLYSIS OF SOME DIPEPTIDES IN ACETIC ACID

By R. J. L. MARTIN\*

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## Summary

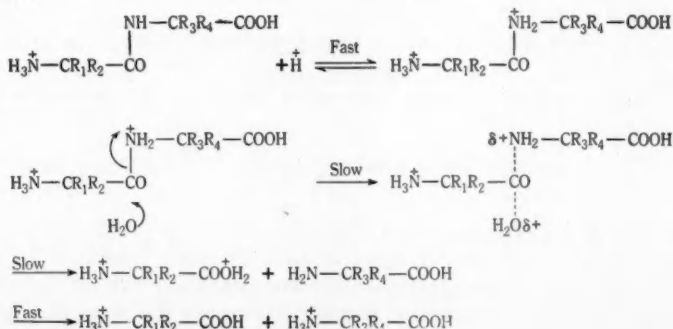
Glycylglycine and a number of its *C*-methyl derivatives have been hydrolysed with excess perchloric acid in aqueous acetic acid as solvent, and by varying the water content of the medium its effect on the reaction rate has been determined. It has been found that small changes in the water concentration cause reversals in the relative rate sequences in both series of dipeptides studied.

In aqueous acetic acid containing more than 2 per cent. water the relative rate sequence in the first series is glycylglycine > alanylglycine >  $\alpha$ -aminoisobutyrylglycine, but at water concentrations less than 2 per cent.  $\alpha$ -aminoisobutyrylglycine reacts faster than glycylglycine. It is concluded that increasing methylation has produced a change in mechanism whereby  $\alpha$ -aminoisobutyrylglycine reacts by a unimolecular heterolysis rather than by the bimolecular mechanism given in the previous paper (Martin 1957).

For the second series of dipeptides, the relative rate sequence is glycylglycine > glycylalanine > glycyl- $\alpha$ -aminoisobutyric acid for water concentrations greater than 2 per cent. At water concentrations less than 2 per cent. the rate sequence is reversed, so that glycyl- $\alpha$ -aminoisobutyric acid > glycylalanine > glycylglycine. This reversal is attributed to changes in the polar effect of the terminal carboxyl group which is brought about by increasing methylation.

## I. INTRODUCTION

The preceding review of published kinetic data has shown that the mechanism of hydrolysis probably consists of an initial fast reversible addition of a proton to the peptide nitrogen. The amide cation so formed reacts at the carbonyl carbon atom with a water molecule in a bimolecular substitution reaction



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Furthermore it appeared that only those substituents at the glycyl carbon atom sterically hindered the substitution by water at the carbonyl carbon atom. On the other hand, there were indications that the steric hindrance of groups on the glycine carbon atom was negligible and that they exert only polar influences.

In this investigation, dipeptides were hydrolysed with excess perchloric acid in aqueous acetic acid of various strengths and the effect of water and increasing methylation on the reaction rate determined. For the two series of dipeptides studied, in which there is increasing methyl substitution at the carbon atoms adjacent to the peptide bond, a reversal in the relative rate sequence has been found for small changes in the water concentration. This has been attributed to changes in the polar factors in one case and a change in the mechanism of reaction in the other case.

## II. RESULTS

For excess perchloric acid, the dipeptide will exist in acetic acid solution as the dipeptide hydroperchlorate. If the concentration of the amide cation is assumed small and proportional to  $[\text{dipeptide HClO}_4][\text{H}^+]$ , since the water concentration is large relative to the dipeptide concentration, the rate of hydrolysis is given by  $k_2[\text{dipeptide HClO}_4][\text{H}^+]$ . For equimolecular quantities of dipeptide and excess acid  $k_2 = x/ta(a-x)$ , where  $a$  is the initial concentration and  $x$  the change in concentration at time  $t$ . The velocity constants calculated from the above equation are given in Tables 1 and 2.

The results in Table 1 show that extremely good sets of bimolecular constants are obtained within a run for glycylglycine. Similar consistent results are also obtained for glycylalanine and alanylglycine. For  $\alpha$ -aminoisobutyrylglycine consistent sets of velocity constants, similar to those given for 0.5 per cent. water in Table 1, are obtained at all water concentrations except 5 per cent. water. At this water concentration the values calculated for the second-order constant increase during the run from  $1.62$  to  $1.87 \times 10^{-4} \text{ sec}^{-1} \text{ g-mol}^{-1} \text{ l}$ , a change of 15 per cent.

A different behaviour is found for glycyl- $\alpha$ -aminoisobutyric acid, and a good set of velocity constants is obtained only at 5 per cent. water (Table 1). At other water concentrations the values calculated for the velocity constant decrease with time and the magnitude of the variation within a run decreases with increasing water concentration.

The bimolecular constant for glycylglycine does not change very much for a twentyfold change in the water concentration and would appear to be independent of the water concentration. For the other dipeptides the rate of reaction decreases with an increasing water concentration.

In the series of compounds  $\begin{array}{c} \text{NH.CH}_2\text{COOH} \\ | \\ \text{CO.CR}_1\text{R}_2\text{NH}_2 \end{array}$ , in which there is increasing methyl substitution at the glycyl carbon atom, the dimethyl derivative reacts either faster or slower than glycylglycine depending upon the water concentration. The monomethyl derivative, alanylglycine, appears to exhibit a similar behaviour but not to the same marked extent.

TABLE I  
DETAILED RESULTS FOR SECOND-ORDER RATE CONSTANTS IN ACETIC ACID AT 120 °C

Glycylglycine 5% water 1% water	$k_2 \times 10^4$ (sec <sup>-1</sup> g-mol <sup>-1</sup> l)	5.78	5.35	5.30	5.42	5.38	5.40	5.36	5.43	5.32	
	Reaction (%)	9	12	17	22	26	31	33	36	73	
	$k_2 \times 10^4$ (sec <sup>-1</sup> g-mol <sup>-1</sup> l)	6.28	6.08	6.08	6.10	6.06	6.00	6.01	5.94	6.01	
	Reaction (%)	14	24	32	39	42	70	72	74	76	
Glycyl - $\alpha$ - aminoiso- butyric acid 5% water 1% water	$k_2 \times 10^4$ (sec <sup>-1</sup> g-mol <sup>-1</sup> l)	1.91	1.85	1.85	1.85	1.84	1.83	1.82	1.84	1.83	
	Reaction (%)	7	12	17	19	22	44	45	47	51	
	$k_2 \times 10^4$ (sec <sup>-1</sup> g-mol <sup>-1</sup> l)	14.5	12.8	11.8	11.0	10.7	10.5	10.3	10.2	10.1	10.0
	Reaction (%)	7	12	16	26	30	35	40	44	50	55
$\alpha$ - Aminoisobutyl- glycine 5% water 1% water	$k_2 \times 10^4$ (sec <sup>-1</sup> g-mol <sup>-1</sup> l)	1.62	1.69	1.69	1.74	1.75	1.83	1.85	1.84	1.84	1.87
	Reaction (%)	5	9	12	16	19	43	46	49	52	65
	$k_2 \times 10^4$ (sec <sup>-1</sup> g-mol <sup>-1</sup> l)	9.52	9.70	9.81	9.81	9.84	9.57	9.64	9.58	9.46	9.31
	Reaction (%)	14	25	34	41	45	78	79	80	81	82



In the series of compounds  $\begin{array}{c} \text{NH.CR}_3\text{R}_4\text{-COOH} \\ | \\ \text{CO.CH}_2\text{NH}_2 \end{array}$ , in which there is successive

methyl substitution at the glycine carbon atom, a similar reversal in the relative rate sequence occurs with changes in the water concentration. Although it has not been possible to calculate a velocity constant to describe the hydrolysis of the dimethyl derivative, it is apparent that it reacts faster than glycylglycine at the lower water concentrations.

The behaviour of glycyl- $\alpha$ -aminoisobutyric acid on hydrolysis seems to indicate a faster reacting impurity but there is every reason to believe that the compound is very pure. Firstly, because the ultimate analysis is correct and secondly, a good set of velocity constants is obtained for 5 per cent. water. It has also been shown that glycine and  $\alpha$ -aminoisobutyric acid are not acetylated under the conditions used in these experiments.

### III. DISCUSSION

#### (a) Mechanism of the Reaction

The interpretation of the results for glycylglycine has already been discussed (Martin 1955, 1957). Noyce and Castelfranco (1951) and Smith and Elliott (1953) have shown that the acidity functions of strong acids in acetic acid decrease with increasing water concentrations. Therefore, for a bimolecular reaction between water and the amide cation, the effect on the reaction rate of an increased water concentration will be counteracted by a decrease in the amide cation concentration so that the observed rate (Table 2) is almost independent of the water concentration.

TABLE 2

SECOND-ORDER VELOCITY CONSTANTS FOR THE HYDROLYSIS OF DIPEPTIDES IN ACETIC ACID AT 120 °C  
 $k_2 \times 10^4 \text{ sec}^{-1} \text{ g-mol}^{-1} \text{ l}$

Water (% by vol) ..	0.25	0.5	1.0	2.0	5.0
Glycylglycine .. ..	$4.86 \pm 4\%$	$5.46 \pm 3\%$ $5.46 \pm 1\%$	$6.14 \pm 3\%$	$6.37 \pm 2\%$	$5.37 \pm 5\%$
Glycylalanine ..		$5.46 \pm 5\%$		$4.54 \pm 2\%$	$3.21 \pm 3\%$
Glycyl - $\alpha$ - aminoiso - butyric acid	20.3 $\rightarrow$ 12.7	11.7 $\rightarrow$ 8.8 14.5 $\rightarrow$ 10.0	7.45 $\rightarrow$ 6.32	4.85 $\rightarrow$ 4.02	1.85 $\pm 2\%$
Alanylglycine ..		$5.16 \pm 2\%$		$4.32 \pm 4\%$	$3.12 \pm 4\%$ $3.20 \pm 3\%$
$\alpha$ -Aminoisobutyryl - glycine	$12.3 \pm 3\%$	$9.62 \pm 3\%$		$3.94 \pm 4\%$	$1.76 \pm 7\%$ $1.73 \pm 7\%$

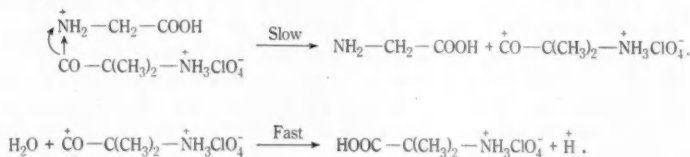
#### (b) Methyl Substitution at the Glycyl Carbon Atom

In a survey of the published kinetic data, Martin (1957) has pointed out that the groups  $R_1$  and  $R_2$  at the glycyl carbon atom will sterically hinder the bimolecular substitution of a water molecule at the carbonyl carbon atom and

there should be a reduction in rate with increasing methylation at the glycyl carbon atom. With acetic acid as solvent, a rate sequence compatible with steric hindrance requirements is observed only at the higher water concentrations. It is most unlikely that the steric hindrance involved in the reaction can be altered by changes in the water concentration, and more probable that increasing methylation has produced changes in either the polar and electrostatic factors or in the mechanism of reaction.

The amount of ion pair formation which occurs in acetic acid would be expected to decrease with an increasing water concentration. Ion pair formation of the perchlorate ion with the positive terminal amino group would reduce the electrostatic effect of this group on the peptide nitrogen and allow the concentration of the amide cation to increase. This effect, however, would operate for all dipeptides and no changes in the relative rate sequence would be expected.

Since the rate of hydrolysis for the dimethyl derivative increases with the hydrogen ion activity, the rate is probably independent of the water concentration and the amide cation is reacting by a rate-controlling unimolecular heterolysis as follows:



The relative rate sequence for 0.5 per cent. water passes through a minimum for increasing methylation and the occurrence of such a minimum usually indicates a change in mechanism (Ingold 1953). The faster rates of hydrolysis of the dimethyl derivative as compared with glycylglycine at the lower water concentrations support a unimolecular heterolysis in so far as there can be no steric hindrance to a unimolecular heterolysis and the electron repelling methyl groups strongly assist the electron transfers necessary for reaction. Ion pair formation will reduce the electron attraction of the terminal amino group and will increase the electron displacements of the methyl groups towards the peptide bond. This unimolecular heterolysis is identical with the mechanism A<sub>AC</sub> 1 (unimolecular acid hydrolysis with acyl-oxygen fission) suggested by Ingold (1953, p. 767) for the hydrolysis of the esters and has the same characteristics, namely, absence of steric retardation and an acceleration by electron repelling groups.

The monomethyl derivative, alanylglycine, exhibits a behaviour intermediate between that for glycylglycine and the dimethyl derivative and it is presumably reacting by mixed order kinetics.

#### (c) Methyl Substitution at the Glycine Carbon Atom

In the preceding paper (Martin 1957), it was shown that substituents at the glycine carbon atom exerted only polar effects and that electron repelling groups reduced the rate of hydrolysis. Increasing methyl substitution at the

glycine carbon atom should therefore reduce the rate of hydrolysis and this has been observed in acetic acid as solvent for water concentrations greater than 2 per cent. At water concentrations less than 2 per cent. there is a reversal in the relative rate sequence and increasing methyl substitution increases, rather than decreases, the rate of hydrolysis. The greater reactivity of glycyl- $\alpha$ -aminoisobutyric acid as compared with glycylglycine at the lower water concentrations definitely indicates the absence of any steric effects for glycine carbon atom substituents, which is in agreement with the findings in the preceding paper. It was also found that, unlike the other dipeptides studied, glycyl- $\alpha$ -aminoisobutyric acid does not hydrolyse by second-order kinetics at the lower water concentrations. In addition, the rate of hydrolysis of glycyl- $\alpha$ -aminoisobutyric acid increases with a decreasing water concentration.

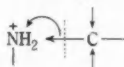
The hydrolysis of glycyl- $\alpha$ -aminoisobutyric acid in acetic acid shows an unexpected behaviour, particularly at the lower water concentrations, and some possible explanations for this follow: (i) solvation; (ii) concentration of amide cation; (iii) change in reaction mechanism; and (iv) polar effect of terminal carboxyl group.

(i) *Solvation*.—Electron repelling groups at the glycine carbon atom have two opposing effects on the reaction rate because they increase the amide cation concentration and hinder the electron transfers necessary for the rupture of the peptide bond. The relative magnitude of these two effects would be expected to change with the nature of the solvent. In acetic acid, a decreasing water concentration would decrease solvation at the positive peptide nitrogen and increase the charge density so that electron repelling groups at the glycine carbon atom would have a smaller effect on reducing the electron transfer to the peptide nitrogen and thus allow hydrolysis to proceed more rapidly. This does not appear to be a satisfactory explanation because at the lower water concentrations the increase in charge density at the peptide nitrogen may be offset by a reduction in charge density brought about by an increase in the ion pair formation at the positive peptide nitrogen. Furthermore, if solvation was the correct explanation then, at the lower water concentrations, the velocity constant of glycyl- $\alpha$ -aminoisobutyric acid would be expected to increase during the run as water was consumed by the reaction.

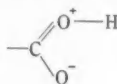
(ii) *Concentration of the Amide Cation*.—Since electron repelling groups at the glycine carbon atom increase the basicity of the peptide nitrogen, then for decreasing water concentrations, glycyl- $\alpha$ -aminoisobutyric acid may form appreciable and increasing amounts of the amide cation at the high acidities which prevail at the low water concentrations. If this is the case it will be necessary to recalculate the velocity constant using corrected concentrations for the amide cation which previously has been assumed to be small and proportional to  $[\text{dipeptide}][\text{HClO}_4][\text{H}^+]$ . Such calculations involving various amounts of amide cation do not give a good set of second-order velocity constants for glycyl- $\alpha$ -aminoisobutyric acid, and it is concluded that this postulate does not explain the behaviour of this compound.

(iii) *Change in Reaction Mechanism*.—The relative rate sequence for increasing methyl substitution at the glycine carbon atom passes through a minimum

at 2 per cent. water or less and such a minimum usually indicates a change in mechanism. In this particular case, a change in mechanism from a bimolecular to a unimolecular heterolysis would be most unlikely because methyl substitution at the glycine carbon atom would tend to retard the reaction by hindering the electron transfers necessary for the rupture of the peptide bond. The inductive effects of methyl groups at the glycine carbon atom would assist an alkyl-nitrogen fission if it occurred (see diagram). Such a reaction would lead to the formation of ammonia which has been shown to be absent in the reaction products. It is concluded that the effects produced in acetic acid as solvent by successive methyl substitution at the glycine carbon atom cannot be accounted for by a change in mechanism:



(iv) *Polar Effect of Terminal Carboxyl Group.*—The glycine carbon atom with its methyl groups is situated between two electron attracting groups, the peptide nitrogen and the terminal carboxyl group, and both these groups will be affected by the electron repelling methyl groups. This extra electron accession to the carboxyl group would assist formation of the resonating structure



If a proton was added to the negative oxygen atom the carboxyl group would be converted into a stronger electron attracting group. This would cause a faster reaction because it was shown in the previous paper (Martin 1957) that electron attracting groups at the glycine carbon atom increase the rate of hydrolysis. A stronger electron attracting group may also be formed from the carboxyl group by hydrogen bonding with an acetic acid molecule. Hydrogen bonding between carboxyl groups is assisted by the above resonating structure (Pauling 1945, p. 307).

Either of these postulates involving the carboxyl group just discussed seems to be the most plausible explanation for the effect on hydrolysis in acetic acid of increasing methylation at the glycine carbon atom. Further work is required before it will be possible to give the correct explanation.

#### IV. EXPERIMENTAL

The acetic acid was purified by the method of Bousfield and Lowry (1911) by refluxing with  $\text{KMnO}_4$  and then fractionally distilling to give a product b.p.  $117.9\text{--}118.0^\circ\text{C}$ , which was stored in a Pyrex flask closed with a magnesium perchlorate tube.

The stock solution of  $0.4\text{N}$  perchloric acid in glacial acetic acid was prepared by dissolving a weighed quantity of analysed AnalaR 72 per cent. perchloric acid in some glacial acetic acid and then adding the correct amount of distilled

acid anhydride to remove all water. The solution was diluted to a known volume at 20 °C with acetic acid.

A 0.04N solution of sodium acetate in glacial acetic acid was prepared from analysed AnalaR sodium acetate trihydrate in the same manner as the perchloric acid solution.

The solution for the kinetic runs was prepared by dissolving sufficient dipeptide to form a 0.05N solution in an aliquot of water (0.25 to 5.0 ml). A 25 ml aliquot of 0.4N perchloric acid was then added and the solution diluted to 100 ml with acetic acid at 20 °C. Aliquots of this solution (7.56 ml) were placed in constricted "Monax" tubes, which were sealed, immersed in an oil thermostat, and shaken. After allowing 12 min for the tubes to reach the required temperature, the first tubes were removed and the reaction time measured from that instant. The reaction was stopped by immediately immersing the tubes in a freezing mixture prepared from crushed solid carbon dioxide and equal volumes of both carbon tetrachloride and chloroform.

For analysis, each tube was crushed under 50 ml of glacial acetic acid and its excess acid was titrated with 0.04N sodium acetate with methyl violet as indicator (Harris 1935; Nadeau and Branchen 1935; Toennies and Callan 1938). Because the coefficient of expansion of acetic acid is large it was necessary to correct all titres to 20 °C.

*Glycylglycine*: B.D.H. glycylglycine which was found to contain a small amount of a faster reacting impurity, probably diketopiperazine, was purified by hydrolysing in water for 15 min at 100 °C with a slight excess of perchloric acid. When the solution had cooled slightly a solution of sodium hydroxide equivalent to the perchloric acid was added; the solution was then filtered and the glycylglycine precipitated by dilution with ethanol.

*Glycyl- $\alpha$ -aminoisobutyric Acid*: This was prepared starting with bromoacetyl bromide and  $\alpha$ -aminoisobutyric acid by the method of Levene, Steiger, and Bass (1929) (Found: C, 45.3; H, 7.5; O, 30.0; N, 16.9; Br <0.3 per cent. Calc. for  $C_6H_{12}N_2O_3$ : C, 45.0; H, 7.6; O, 30.0; N, 17.5 per cent). Attempts to prepare glycyl- $\alpha$ -aminoisobutyric acid by the method of Boissonnas (1951) using *N*-phthaloylglycine were unsuccessful. For this attempted preparation, phthaloylglycine (0.25 mole) (prepared by the method of Billmann and Harting 1948 and Sheehan and Frank 1949) and triethylamine (0.25 mole) were dissolved in 600 ml acetone and after cooling to 0 °C, ethyl chloroformate (0.25 mole) was added in small quantities at a time with vigorous stirring. A solution of  $\alpha$ -aminoisobutyric acid (0.25 mole) and sodium hydroxide (0.25 mole) in 30 ml water were then added with stirring to the cold acetone solution of the mixed anhydride. Acidifying and removing the acetone under vacuum resulted in recovery of the starting material phthaloylglycine.

*Glycylalanine, Alanylglycine, and  $\alpha$ -Aminoisobutyrylglycine*: The carbobenzoxy dipeptide esters needed for the preparation of these dipeptides were obtained by the mixed anhydride method of Boissonnas (1951). Anhydrous conditions were used in chloroform as solvent. The carbobenzoxy-derivatives of the amino acids were prepared according to the method of Bergmann and

Zervas (1932). The carbobenzoxy-derivative (0.2 mole) and triethylamine (0.2 mole) were dissolved in 350 ml of anhydrous chloroform and the solution cooled to  $-5^{\circ}\text{C}$ . Ethyl chloroformate (0.2 mole) was added to the chloroform solution in one lot and the reaction mixture allowed to stand at  $0^{\circ}\text{C}$  for 30 min. A precooled solution of the amino acid ethyl ester hydrochloride (0.2 mole) and triethylamine (0.2 mole) in 170 ml of chloroform was added in one lot to the reaction mixture. After being kept for 2 hr at  $0^{\circ}\text{C}$ , the reaction mixture was allowed to reach room temperature overnight. Subsequently the chloroform solution was refluxed, then cooled and washed successively with water, 3 per cent.  $\text{NaHCO}_3$  solution, water, dilute hydrochloric acid, and water. Without drying, the chloroform was distilled under reduced pressure. The resulting carbobenzoxy dipeptide ester was hydrolysed with alkali without further purification and the carbobenzoxy-group removed from the dipeptide by hydrogenation with palladium black (Bergmann *et al.* 1935). The  $\alpha$ -aminoisobutyrylglycine was crystallized from warm aqueous ethanol by first dissolving the peptide in a small amount of water and then adding warm ethanol (Found: C, 45.0; H, 7.5; O, 29.9; N, 17.7 per cent. Calc. for  $\text{C}_6\text{H}_{12}\text{N}_2\text{O}_3$ : C, 45.0; H, 7.6; O, 30.0; N, 17.5 per cent).

Attempts to prepare  $\alpha$ -aminoisobutyrylglycine by the phthaloyl method described above were unsuccessful. Phthaloylglycylalanine was prepared by this method but the product was extremely difficult to purify.

#### V. ACKNOWLEDGMENTS

The author thanks Dr. J. M. Swan and Mr. A. F. Beecham for the helpful advice given for the preparation of the dipeptides.

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# IONIZATION OF PICRIC ACID IN METHANOL TO 3000 ATM

By W. STRAUSS\*

[Manuscript received December 14, 1956]

## Summary

Electrical conductances of methanolic solutions of a number of salts, picric acid, and hydrobromic acid have been measured to 3000 atm at 25 °C. Two mechanisms, proton transfer and movement of  $\text{CH}_3\text{OH}_2^+$  ions, contribute to the conductance of  $\text{H}^+$  ions in methanol. Some suggestions concerning the proton transfer mechanism in both water and methanol at high pressure are made. The data have also been used to calculate the ionization constant, free energy, and molar volume change of ionization of picric acid in methanol to 3000 atm.

## I. INTRODUCTION

Hamann and Strauss (1956) have previously reported measurements of the effect of pressure on the ionization of a weak base, piperidine, in methanol. The present paper describes similar measurements on the ionization of a weak acid, picric acid, in methanol. The electrical conductances of solutions of picric acid, hydrobromic acid, sodium picrate, and sodium bromide and chloride in methanol have been measured to pressures of 3000 atm at 25 °C, and have been used to derive the ionization constant, free energy of ionization, and molar volume change for the ionization of picric acid.

## II. EXPERIMENTAL

(i) *Apparatus*.—The equipment used was that described by Buchanan and Hamann (1953).

(ii) *Materials*.—B.D.H. AnalaR picric acid was recrystallized several times from methanol and carefully dried. Sodium picrate solution was prepared by titrating a measured quantity of picric acid solution of known concentration, with sodium methoxide solution of known concentration, checking the end-point with an external indicator. HBr gas was made by adding aqueous HBr dropwise to phosphorus pentoxide, and the methanolic solutions of HBr were prepared by dissolving the gas in dry methanol after passing it through a drying train consisting of a series of U-tubes surrounded by a dry ice/alcohol mixture. The solutions were standardized against barium hydroxide. Analytical grades of sodium chloride and bromide were used, after careful drying, without further purification. The preparation of pure dry methanol has been previously described (Hamann and Strauss 1956).

The experimental procedure, and the sources and magnitudes of the inaccuracies have been discussed by Buchanan and Hamann (1953).

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## III. RESULTS AND DISCUSSION

## (a) Conductances

The conductance of each electrolyte was measured for a range of concentrations and pressures. The *molar* conductances  $\Lambda'$  were calculated from the relation

$$\Lambda' = 1000\kappa/c,$$

where  $\kappa$  is the specific conductance in  $\text{cm ohm}^{-1}$ , corrected for the contribution of the solvent, and  $c$  the concentration of the electrolyte in  $\text{mole kg}^{-1}$ . Typical values of the *molar* conductances are listed in Table 1. Their trends are similar to those found in earlier work (Hamann and Strauss 1956), except for the conductances of HBr, which call for special comment.

TABLE 1  
MOLAL CONDUCTANCES IN METHANOL AT 25 °C TO 3000 ATM  
 $\text{cm g ohm}^{-1} \text{mole}^{-1}$

Pressure (atm)	Picric Acid 0.0114m†	Sodium Picrate 0.00988m	HBr 0.0028m	NaCl 0.00919m	NaBr* 0.00137m
1	20.5	56.8	127.7	60.9	71.5
1000	29.1	43.7	116.1	51.5	59.0
2000	34.3	37.1	107.8	45.5	51.5
3000	37.6	32.4	101.0	40.5	44.8

\* Hamann and Strauss (1956).

† m, concentration as  $\text{mole kg}^{-1}$ .

The compression of methanol at 25 °C was obtained by linear interpolation of the experimental data at 20 °C by Bridgman (1949) and at 30 °C by Stutchbury (1956). From the densities of compressed methanol and the *molar* conductances, the more usual molar conductances were found. These were insufficient to

TABLE 2  
CONDUCTANCES OF 0.0025M SOLUTIONS IN METHANOL AT 25 °C TO 3000 ATM  
 $\text{cm}^2 \text{ohm}^{-1} \text{mole}^{-1}$

Pressure (atm)	Sodium Picrate	HBr	NaCl	NaBr	$\lambda^+ = \text{HBr} - \text{NaBr}$
1	80.4	162	84.3	87.3	75
1000	57.7	137	65.7	68.5	69
2000	47.5	121	54.5	56.3	65
3000	39.2	110	46.7	48.2	62

extrapolate accurately to infinite dilution; instead the molar conductances of 0.0025M solutions, which are within the experimental range, are given in Table 2.

The abnormally high conductance of strong acids in water and organic alcohols is accounted for by a proton transfer mechanism. It has been effectively



demonstrated (Gierer and Wirtz 1949; Conway, Bockris, and Linton 1956) that in water, although the rapid proton interchange precludes any permanent  $\text{H}_3\text{O}^+$  entity, the  $\text{H}_3\text{O}^+$  ion does exist, because a proton spends a much longer time with a definite water molecule than as a proton migrating. It has been assumed by these workers that the  $\text{H}_3\text{O}^+$  ion conductance is approximated by that of an alkali ion  $\text{X}^+$ , and the excess conductance due to the proton transfer mechanism can be estimated by

$$\lambda^+ = \lambda_{\text{H}^+} - \lambda_{\text{X}^+} = \Lambda_{\text{HA}} - \Lambda_{\text{XA}}$$

The excess molar conductance in water, calculated from the *molar* conductances of HCl and KCl measured to pressures of 12,000 atm (Hamann and Strauss 1955), first increases steeply, reaching a maximum between 8000 and 10,000 atm, and then decreases slightly. Hamann and Strauss (1955), adopting Bell's (1941) model for proton transfer, suggested that pressure assists proton exchange as it provides some of the repulsion energy needed to bring the oxygen close enough for a proton switch to occur. More recently, Conway, Bockris, and Linton (1956) have shown that the rate-determining step in the proton transfer mechanism is the rotation of the hydrogen-bonded water molecules near the  $\text{H}_3\text{O}^+$  ion. The present author suggests that very high pressures hinder this rotation, introducing a deterrent to proton transfer, which would account for the maximum value.

In methanolic solutions, HBr shows a steady decrease in *molar* conductance with increasing pressure, but this decrease is not as great as for methanolic solutions of strong salts. An estimate of the contribution of the  $\text{H}^+$  ion to the *molar* conductance of the methanolic HBr has therefore been made by subtracting the contribution of the  $\text{Br}^-$  ion from the measured *molar* conductances of HBr. The contribution of the  $\text{Br}^-$  ion has been estimated by assuming, firstly, that its contribution to the conductance of HBr is the same as its contribution to the conductance of a strong salt such as NaBr at the same concentration, temperature, and pressure; and secondly, that the relative contribution of the  $\text{Br}^-$  ion to the conductance of a strong salt in methanol does not vary with concentration or pressure. The molar conductances of the  $\text{Na}^+$  and  $\text{Br}^-$  ions in methanol at 25°C, atmospheric pressure, and at infinite dilution have been taken from Gordon *et al.* (1953). The *molar* conductance ratios,  $\Lambda_p/\Lambda_i$ , for NaCl, NaBr, sodium picrate, picric acid, HBr, and the  $\text{H}^+$  ion are plotted in Figure 1.

The curve for the  $\text{H}^+$  ion shows that its *molar* conductance decreases slightly with increasing pressure. A similar plot of molar conductances would emphasize this. The last column in Table 2 lists the excess conductance  $\lambda^+$  of the  $\text{H}^+$  ion in methanol. In water, the excess conductance accounts for about 80 per cent. of the  $\text{H}^+$  ion conductance at atmospheric pressure, but in methanol, only about 66 per cent., the remainder being due to  $\text{CH}_3\text{OH}_2^+$  ions. This agrees with Conway, Bockris, and Linton's (1956) finding that the excess proton conductance decreases with increasing  $n$  in the series  $\text{C}_n\text{H}_{2n+1}\text{OH}$ . In methanol, the values of the excess molar conductance decrease with increasing pressure over the measured range. This can be explained by an extension

of the argument used for water at much higher pressures: that the hindering of rotation of the hydrogen-bonded methanol molecules, more effective with the larger solvent molecules under pressure, will deter proton transfer.

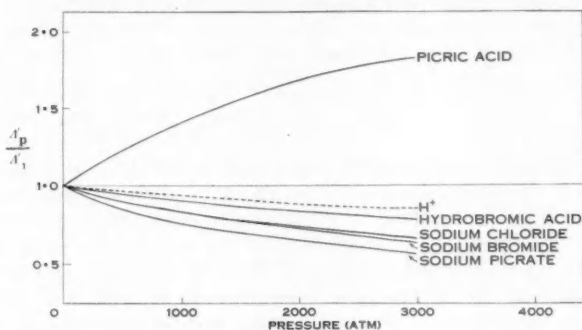


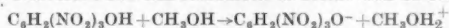
Fig. 1.—Ratios of molal conductances of electrolytes in methanol to 3000 atm at 25 °C.

(b) Ionization Constant

The acidic ionization constant  $K$  of picric acid has been calculated in the manner described previously (Buchanan and Hamann 1953); in methanol at 25 °C it increases from  $2.64 \times 10^{-4}$  mole kg $^{-1}$  at 1 atm to  $22.4 \times 10^{-4}$  mole kg $^{-1}$  at 3000 atm. This is a considerably greater change than was found for aqueous formic acid.

TABLE 3

THERMODYNAMIC FUNCTIONS FOR THE IONIZATION OF PICRIC ACID IN METHANOL AT 25 °C



Pressure (atm)	1	1000	2000	3000
$K \times 10^4$ (mole kg $^{-1}$ ) .. ..	2.64 (2.32)*	6.59	13.31	22.4
$\Delta G^\circ$ (cal mole $^{-1}$ ) .. ..	4880	4340	3920	3620
Pressure (atm)	1	500	1500	2500
$\Delta V^\circ$ (cm $^3$ mole $^{-1}$ ) .. ..	-25.0†	-22.3	-17.2	-12.7

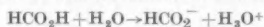
\* MacInnes (1939), calculated from experimental data by Goldschmidt.

† Value obtained by graphical extrapolation.

The free energy of ionization  $\Delta G^\circ$  and the molal volume change  $\Delta V^\circ$  have been calculated from the usual thermodynamic formulae. Values of  $K$ ,  $\Delta G^\circ$ , and  $\Delta V^\circ$  for picric acid in methanol are listed in Table 3, while for comparison the corresponding functions for aqueous formic acid (Hamann and Strauss 1955) are listed in Table 4.

TABLE 4\*

THERMODYNAMIC FUNCTIONS FOR THE IONIZATION OF FORMIC ACID IN WATER\* AT 25 °C



Pressure (atm)	1	1000	2000	3000
$K \times 10^4$ (mole kg <sup>-1</sup> ) .. ..	1.73	2.44	3.25	4.18
$\Delta G^\circ$ (cal mole <sup>-1</sup> ) .. ..	5130	4930	4760	4610
Pressure (atm)	1	500	1500	2500
$\Delta V^\circ$ (cm <sup>3</sup> mole <sup>-1</sup> ) .. ..	-8.8†	-8.23	-7.04	-6.15

\* Hamann and Strauss (1955).

† Value obtained by graphical extrapolation.

## IV. ACKNOWLEDGMENTS

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# THE FORMATION OF THE HEXABROMOPALLADATE(II) ION

By C. M. HARRIS,\* S. E. LIVINGSTONE,\* and I. H. REECE\*

[Manuscript received March 3, 1957]

## Summary

Spectrophotometric studies on nitrobenzene solutions containing the tetrabromopalladate(II) ion and bromide ions demonstrate the formation of an unstable hexabromopalladate(II),  $[\text{PdBr}_6]^{4-}$ , ion. The possible structure of this six-covalent complex is discussed.

## I. INTRODUCTION

We have observed that the extinction coefficient of the tetrabromopalladate (II) ion ( $\epsilon=2750$  at  $427 \text{ m}\mu$ ) in nitrobenzene solution is lowered by the addition of bromide ions (see Fig. 1). A similar phenomenon has recently been reported by Sundaram and Sandell (1955) in the case of tetrachloropalladate(II) ion and chloride ions in aqueous solutions containing perchloric acid to repress

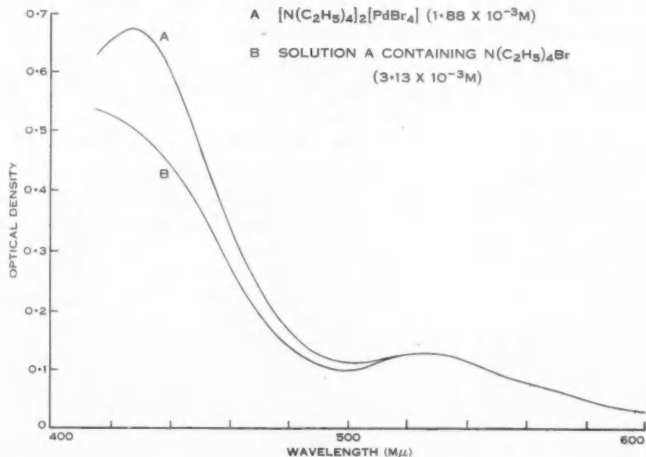


Fig. 1.—Absorption spectrum of nitrobenzene solution of tetrabromopalladate(II) ion in 1.24 mm cell.

hydrolysis. These workers suggested that their results indicated the possible existence of the higher complexes  $[\text{PdCl}_5]^{3-}$  and  $[\text{PdCl}_6]^{4-}$ . Sundaram and Sandell did not succeed in establishing the composition of any complexes containing more than four chlorine atoms per palladium atom.

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In nitrobenzene solution the  $[\text{PdBr}_4]^{2-}$  ion possesses a broad absorption band with a maximum at  $427 \text{ m}\mu$  (Fig. 1). By using a differential spectrophotometric method (see Section II) it has been possible to carry out a continuous variation study at this wavelength on mixtures of  $5 \times 10^{-3} \text{ M}$  nitrobenzene solutions of tetraethylammonium tetrabromopalladate(II) and tetraethylammonium bromide. A maximum optical density difference (Fig. 2) occurs at a 2:1 ratio of bromide ions to tetrabromopalladate(II) ions. This demon-

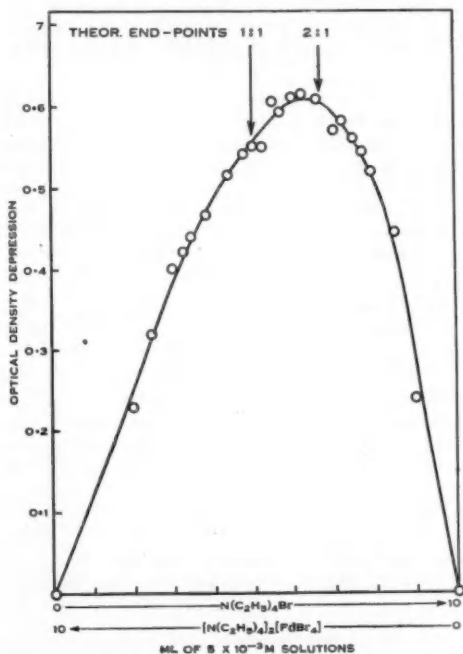


Fig. 2.—Continuous vibration study on nitrobenzene solutions of tetraethylammonium tetrabromopalladate(II) and bromide ions at  $427 \text{ m}\mu$  in  $5.00 \text{ mm}$  cell at  $25^\circ \text{C}$ .

strates the formation of the hexabromopalladate(II) ion,  $[\text{PdBr}_6]^{4-}$ , in this solvent. Although a number of attempts were made to isolate the salt  $[\text{N}(\text{C}_2\text{H}_5)_4]_4[\text{PdBr}_6]$  from nitrobenzene solution the original compound  $[\text{N}(\text{C}_2\text{H}_5)_4]_2[\text{PdBr}_4]$  was always recovered. This study failed to reveal any evidence for the existence of the  $[\text{PdBr}_5]^{3-}$  ion. Nitrobenzene was used as a solvent rather than water in order to remove the possibility of hydrolysis and also to reduce the energy of solvation of the bromide ions.

## II. EXPERIMENTAL

## (a) Materials

The tetraethylammonium bromide (B.D.H. laboratory reagent) was thoroughly dried over phosphoric oxide and nitrobenzene was purified by freezing and fractionating from phosphoric oxide. The tetraethylammonium tetrabromopalladate(II) complex was prepared by refluxing tetraethylammonium tetrabromo- $\mu\mu'$ -dibromodipalladate(II) with tetraethylammonium bromide in aqueous acetone.

(i) *Tetraethylammonium Tetrabromo- $\mu\mu'$ -dibromodipalladate(II)*.—This compound, first described by Gubtier and Fellner (1916), was prepared as follows: Potassium tetrabromopalladate(II) (3.0 g) dissolved in water (50 ml) was added to an aqueous solution of tetraethylammonium bromide (1.6 g). The resulting precipitate was filtered off and recrystallized from 1:1 acetone-ethanol (100 ml) to give shining brown plates (1.8 g) (Found: C, 20.4; H, 4.4; N, 2.7; Br, 49.5; Pd, 22.4%. Calc. for  $C_{16}H_{40}N_2Br_6Pd_2$ : C, 20.2; H, 4.2; N, 2.9; Br, 50.2; Pd, 22.4%).

(ii) *Tetraethylammonium Tetrabromopalladate(II)*.—A solution of tetraethylammonium tetrabromo- $\mu\mu'$ -dibromodipalladate(II) (0.70 g) in boiling acetone (100 ml) was poured into a solution of tetraethylammonium bromide (2.5 g) in boiling acetone (150 ml) containing water (5 ml). After a few minutes at the boiling point pinkish brown crystals of the compound began to separate; after a further 10 min on the steam-bath, the mixture was filtered, and the product washed well with acetone; yield 0.82 g. The compound is insoluble in cold water and acetone but moderately soluble in nitrobenzene (Found: C, 27.8; H, 6.2; N, 3.9; Br, 46.5; Pd, 15.5%. Calc. for  $C_{16}H_{40}N_2Br_4Pd$ : C, 28.0; H, 5.9; N, 4.1; Br, 46.5; Pd, 15.5%).

## (b) Solutions

Stock solutions of tetraethylammonium bromide ( $5 \times 10^{-3}M$ ) and tetraethylammonium tetrabromopalladate(II) ( $5 \times 10^{-3}M$ ) were made up in pure nitrobenzene. Gentle heating was used to hasten solution. Appropriate dilutions were made volumetrically with these two solutions.

Two series of solutions were prepared for examination: an "A" series containing the  $[PdBr_4]^{2-}$ :  $Br^-$  ratios indicated on the curve in Figure 2, as well as a "B" series of identical  $[PdBr_4]^{2-}$  concentrations without added bromide. The difference in optical density between corresponding solutions of the same  $[PdBr_4]^{2-}$  concentration in the A and B series was measured by a differential spectrophotometric method as described in Section II (c). The decrease in optical density due to the effect of added bromide ions on the extinction coefficient of the tetrabromopalladate(II) ion is plotted against the  $[PdBr_4]^{2-}$ :  $Br^-$  ratios in Figure 2.

The tetrabromopalladate(II) ion was shown to obey Beer's law at 427 m $\mu$  over the concentration range studied and the extinction coefficient of this ion was found to be 2750 at this wavelength.

## (c) Spectrophotometric Measurements

All optical density measurements were made on a Cary recording spectrophotometer at  $25 \pm 0.5^\circ C$ . In order to obtain optical density depressions in the range 0.1 to 0.6 it was necessary to use  $[PdBr_4]^{2-}$  solutions with optical densities as high as 6 in a 5.00 mm cell. The optical density differences were measured by the following differential method.

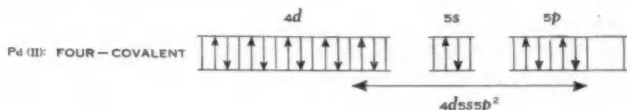
Corresponding A and B solutions (i.e. solutions of identical  $[PdBr_4]^{2-}$  concentration) in matched cells were compared with a suitable reference cell (0.5–3.0 cm) containing nitrobenzene. The reference cell was chosen so that its optical density was within 1 to 2 density units of the sample density. In this way suitable pen deflections were obtained for these solutions. The difference in pen deflections gave the optical density depression due to added bromide.

Care was necessary to avoid the spurious effects of scattered radiation so the slit controlling device was not used in the normal way as for scanning; rather, the slit width was kept constant at 0.15 mm (c. 11 Å total band-pass) while the instrument sensitivity was varied accordingly. All measurements were recorded on the chart and where the gain and consequently the noise level was high, longer traces were made to ensure a reasonable reading accuracy.

All solutions were equilibrated at 25.0 °C for 2 days before measurement and were kept in an anhydrous atmosphere. Various pairs of solutions were checked over a period of a few days and were found to be constant in optical density difference. The overall experimental error is of the order of 5 per cent.

### III. DISCUSSION

Divalent palladium and platinum normally form four-covalent square-planar complexes. This is regarded as arising from  $4d5s5p^2$  hybridization at the metal atom in the case of palladium:



A few compounds have been reported (see Sidgwick 1950) in which it is suggested that the palladium(II) atom is six-covalent. These compounds have been little investigated and their structures are unknown.

Recently, Harris and Nyholm (1956) have prepared a series of apparently four-, five-, and six-covalent complexes of divalent palladium with the chelate group *o*-phenylenebis(dimethylarsine)(diarsine). A structural investigation (Harris, Nyholm, and Stephenson 1956) of the diiodide,  $\text{Pd}(\text{diarsine})_2\text{I}_2$ , has shown

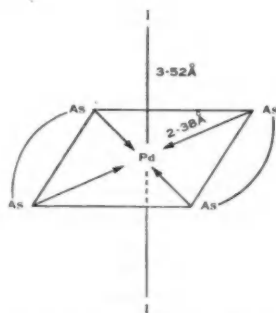


Fig. 3.—The distorted octahedral arrangement of the diiodo-di(*o*-phenylenebis(dimethylarsine))palladium(II) molecule.

that this substance exists as discrete molecules in the solid state and that the palladium atom possesses the distorted octahedral arrangement shown in Figure 3. It is suggested that the grossly elongated Pd—I bonds result from linear  $5p5d$  bonds perpendicular to the square  $4d5s5p^2$  arrangement of the palladium-arsenic plane.

The unstable hexabromopalladate(II) ion can also be regarded as arising from this special kind of bonding. This ion would most likely possess a tetragonal structure also with elongated bonds in the *trans*-octahedral positions. It is

interesting to note in this connection that Jørgensen (1956) has recently predicted that palladium in a  $d^8$ -configuration ( $^1\Gamma_3$  state) should be subject to Jahn-Teller distortion.

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## A STUDY ON MAGNESIUM OXYSULPHATES

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### Summary

The reactions which take place in the system  $\text{MgO-MgSO}_4\text{-H}_2\text{O}$  at concentrations of  $\text{MgSO}_4$  solutions up to saturation and temperatures from 30 to 120 °C have been studied in detail. Four oxysulphates have been found, namely,  $5\text{Mg}(\text{OH})_2\cdot\text{MgSO}_4\cdot 3$  or  $2\text{H}_2\text{O}$ ,  $3\text{Mg}(\text{OH})_2\cdot\text{MgSO}_4\cdot 8\text{H}_2\text{O}$ ,  $\text{Mg}(\text{OH})_2\cdot\text{MgSO}_4\cdot 5\text{H}_2\text{O}$ , and  $\text{Mg}(\text{OH})_2\cdot 2\text{MgSO}_4\cdot 3\text{H}_2\text{O}$ , and an equilibrium diagram has been prepared which gives the conditions at which each is stable. X-Ray diffraction powder patterns of each of the oxysulphates are given and the stabilities of the compounds are briefly discussed.

### I. INTRODUCTION

Demediuk (1952) and Demediuk and Hosking (1955) have shown that unsoundness in magnesian limes can be reduced by the addition of magnesium chloride or magnesium sulphate, but that magnesium chloride was the more effective of the two. It was believed that the reduction was due to the formation of stable magnesium oxychlorides or oxysulphates, so Demediuk, Cole, and Hueber (1955) studied the system  $\text{MgO-MgCl}_2\text{-H}_2\text{O}$  to determine the conditions under which oxychlorides form. In the present paper an account is given of a parallel study of the system  $\text{MgO-MgSO}_4\text{-H}_2\text{O}$ .

Although Thugutt (1892) had prepared a magnesium oxysulphate by heating a mixture of sodium hydroxide, magnesium sulphate, and water at 200 °C, little was known about these compounds until more than 40 years later when Aspelund (1933) reported the preparation of  $3\text{Mg}(\text{OH})_2\cdot\text{MgSO}_4\cdot 8$  or  $9\text{H}_2\text{O}$  (later prepared by Delyon (1936) and Walter-Lévy (1936a) with  $8\text{H}_2\text{O}$ ). Since the paper by Aspelund is not available to us we do not know his method of preparation, but Delyon obtained the 3-form of oxysulphate by dissolving at 80°,  $\text{MgO}$  in a magnesium sulphate solution of 500 g/l of the heptahydrate. Walter-Lévy (1936a) in studying basic magnesium sulphocarbonate, obtained from the cold mother liquor of this compound a precipitate which was a mixture of magnesium sulphate and  $3\text{Mg}(\text{OH})_2\cdot\text{MgSO}_4\cdot 8\text{H}_2\text{O}$ . In a further study Walter-Lévy (1936b) obtained, with long boiling, the compound  $5\text{Mg}(\text{OH})_2\cdot\text{MgSO}_4\cdot 3\text{H}_2\text{O}$  from solutions of magnesium sulphate to which had been added potassium bicarbonate. At a temperature of 150° the compound had two molecules of water only. After a shorter period of boiling it was found that the chilled solution precipitated a mixture of  $3\text{Mg}(\text{OH})_2\cdot\text{MgSO}_4\cdot 8\text{H}_2\text{O}$  and  $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ . Walter-Lévy also repeated the experiment of Thugutt (1892) and obtained material which gave the X-ray pattern of the 5-form; Thugutt's

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analysis indicated a mixture of  $\text{Mg}(\text{OH})_2$  and  $6\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$ . Feitknecht (1933) published the X-ray powder pattern of a basic magnesium oxysulphate, which we identify as the 5-form, and suggested that it had a layer structure like other oxy-salts he had investigated.

In the present work, the system  $\text{MgO}-\text{MgSO}_4-\text{H}_2\text{O}$  is investigated in more detail than hitherto. The reactions are studied by examining, by chemical, X-ray, and differential thermal methods, the composition of the products formed at concentrations of  $\text{MgSO}_4$  up to saturation and temperatures from 30 to 120 °C. Four oxysulphate compounds have been recognized, namely  $5\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 3$  or  $2\text{H}_2\text{O}$ ,  $3\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 8\text{H}_2\text{O}$ ,  $\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 5\text{H}_2\text{O}$ , and  $\text{Mg}(\text{OH})_2 \cdot 2\text{MgSO}_4 \cdot 3\text{H}_2\text{O}$ , and the stability fields of each delineated.

## II. EXPERIMENTAL PROCEDURE

The compounds formed by reaction between magnesium oxide (light; B.D.H. laboratory reagent) and magnesium sulphate (analytical reagent) solutions at various concentrations were obtained by allowing 1 g of solid to react with 100 ml of solution, in a manner similar to that used by Delyon (1936) at temperatures of 30, 40, 45, 50, 70, 80, 90, 100, 110, and 120 °C.

The solutions of magnesium sulphate were prepared at room temperature ( $\sim 20$  °C) and those up to 33 per cent. weight/volume (the solubility of magnesium sulphate heptahydrate in water at 20 °C) were made by diluting a saturated stock solution. Those above 33 per cent. were made by adding calculated quantities of water to weighed amounts of magnesium sulphate heptahydrate. In this procedure the specific gravity of magnesium sulphate heptahydrate at 20 °C was taken as 1.678 and it was assumed that this compound occupied the same volume when dissolved as it did in the solid state. Separate experiments indicated that this is true within the limits of accuracy of the work. The solution concentration obtained in this way can be expressed as weight/volume (with such units results can be compared directly with those of earlier workers). However, it is possible to express the solution concentrations as weight/weight and avoid the assumption made above. As a consequence the solution concentrations are given in Figure 1 both as percentage weight/volume and percentage weight/weight. A conversion graph was constructed using density data from International Critical Tables (1928, Vol. 3, p. 72) up to concentrations of 26 per cent. weight/volume and beyond this, calculations of weight/volume from weight/weight values using 1.678 as the density of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  (solid) and the same assumption as above.

In initial experiments, a series of replicates were analysed in turn after specified intervals of time to find the required time needed to reach equilibrium, since this varies with the temperature of the solution. It was 7 days at a temperature of 30 °C and 24, 20, and 16 hr at temperatures of 90, 100, and 120 °C, respectively. In subsequent experiments times longer than these were always used. At the end of these periods most mixtures were filtered rapidly and washed with hot anhydrous methanol. When large quantities of material were required the purification was carried out in a Soxhlet extractor using methanol as the extracting solvent.

In washing precipitates formed at and above 70 °C from solutions of high concentration of  $\text{MgSO}_4$  difficulties were experienced because the methanol precipitated lower hydrates of magnesium sulphate. Some of these (unlike magnesium sulphate heptahydrate) are practically insoluble in methanol and the monohydrate is even barely soluble in water. To overcome this difficulty sufficient magnesium sulphate solution (25 per cent.) was added to the contents

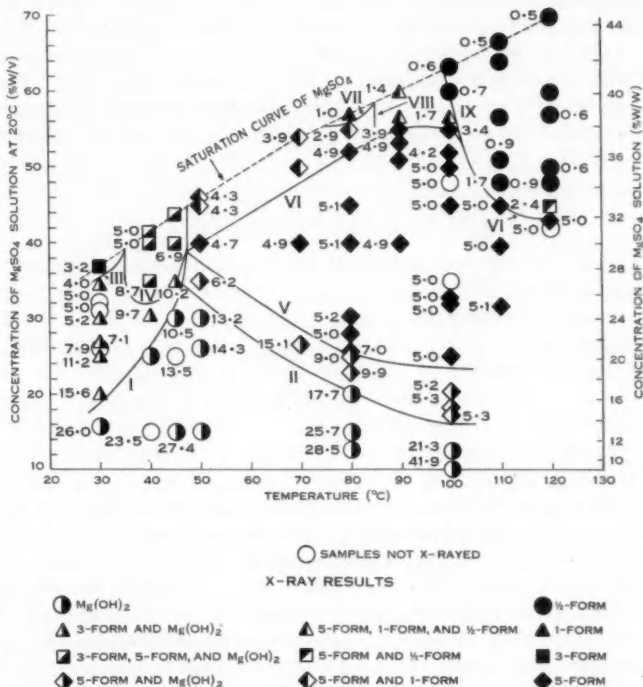


Fig. 1.—Phase equilibria in the system  $\text{MgO-MgSO}_4\text{-H}_2\text{O}$ . The  $\text{Mg}(\text{OH})_2 : \text{MgSO}_4$  ratio (where determined) is given for precipitates found at different conditions of temperature and concentration of  $\text{MgSO}_4$  solution. Curve III, conditions for formation of pure  $3\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot x\text{H}_2\text{O}$ ; V, pure  $5\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot x\text{H}_2\text{O}$ ; VII, pure  $\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot x\text{H}_2\text{O}$ ; IX, pure  $\text{Mg}(\text{OH})_2 \cdot 2\text{MgSO}_4 \cdot x\text{H}_2\text{O}$ ; I, II, IV, VI, VIII define boundaries of mixed phases.

of the flask after the reaction was complete to reduce the concentration of the mother liquor to a value at which methanol no longer precipitated the lower hydrates. The contents of the flask were shaken gently and the suspension was then poured off, leaving the coarsely crystalline solid magnesium sulphate adhering to the walls and bottom of the flask. The precipitate recovered from the suspension was washed with methanol in the usual way.

Originally all reaction products were kept in a vacuum desiccator over solid NaOH, but at a later stage they were simply placed in stoppered bottles since it was found that they were unaffected by the atmosphere. They were analysed by chemical and X-ray methods and a selected few, in which amorphous precipitates had formed at low concentrations, were examined by the differential thermal method. In the chemical analyses, MgO was determined volumetrically by titration with versenate (disodium salt of ethylenediaminetetra-acetic acid) after the method of Cheng, Kurtz, and Bray (1952),  $\text{SO}_4^{2-}$  gravimetrically by precipitation as  $\text{BaSO}_4$  according to the procedure of Cumming and Kay (1948, p. 247), and  $\text{H}_2\text{O}$  by difference. The X-ray photographs were taken with copper radiation filtered by nickel foil in a Unicam single crystal camera of radius 3.00 cm which had been modified to record spacings as high as 20 kX. The differential thermal analyses were made with equipment described by Carthew and Cole (1953).

### III. RESULTS AND DISCUSSION

#### (a) Phases in the System $\text{MgO-MgSO}_4\text{-H}_2\text{O}$

The results for the system  $\text{MgO-MgSO}_4\text{-H}_2\text{O}$  are illustrated graphically in Figure 1, where the  $\text{Mg}(\text{OH})_2$  to  $\text{MgSO}_4$  ratio of the reaction product is given for each of the solution concentrations and temperatures studied. In Figure 1, no account has been taken of the number of water molecules associated with each reaction product and in the discussion that follows this has been left indeterminate (expressed as  $x\text{H}_2\text{O}$ ) although finally it is indicated that each form has a definite number of water molecules. The results show that the system  $\text{MgO-MgSO}_4\text{-H}_2\text{O}$  is more complex than the analogous system  $\text{MgO-MgCl}_2\text{-H}_2\text{O}$  (Demediuk, Cole, and Hueber 1955) studied over the same temperature range.

In constructing Figure 1, boundary lines between phases are in general based on the X-ray diffraction results, since in some instances  $\text{MgSO}_4$  may be trapped in the precipitate or be present in a relatively insoluble form. Thus the curves I and II defining the upper limit at which  $\text{Mg}(\text{OH})_2$  occurs alone are determined on X-ray evidence and disregard the small amounts of  $\text{MgSO}_4$  detected by chemical analysis. The presence of this  $\text{MgSO}_4$  was confirmed by differential thermal analysis, which also indicated that it had not reacted with the  $\text{Mg}(\text{OH})_2$  to form an amorphous oxysulphate, but was probably absorbed by the bulky gel-like precipitate of  $\text{Mg}(\text{OH})_2$  from which it could not be removed by washing with methanol. The absorption of  $\text{MgSO}_4$  by a  $\text{Mg}(\text{OH})_2$  gel has also been noted by Kiesewetter (1953). However, Demediuk, Cole, and Hueber (1955) found that in the system  $\text{MgO-MgCl}_2\text{-H}_2\text{O}$ ,  $\text{MgCl}_2$  was not absorbed by a  $\text{Mg}(\text{OH})_2$  gel but reacted to form an amorphous oxychloride. It will be noted in Figure 1 that the curves I and II form a peak at about 45 °C where there is a markedly higher concentration of  $\text{MgSO}_4$  solution, compared with that at other temperatures at which crystalline oxysulphates first appear.

At concentrations of  $\text{MgSO}_4$  higher than those defined by curves I and II, the fields show mixtures of  $\text{Mg}(\text{OH})_2$  and crystalline oxysulphates, and above those defined by curves III and V, the pure oxysulphates occur. The type of oxysulphate that forms depends on both the concentration of the  $\text{MgSO}_4$  solution

and the temperature. Thus immediately above curves I and II with increasing temperature we have the following fields: (1)  $\text{Mg}(\text{OH})_2 + 3\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot x\text{H}_2\text{O}$ ; (2)  $\text{Mg}(\text{OH})_2 + 3\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot x\text{H}_2\text{O} + 5\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot x\text{H}_2\text{O}$ ; and (3)  $\text{Mg}(\text{OH})_2 + 5\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot x\text{H}_2\text{O}$ . The 3-form of oxysulphate is only stable at low temperatures and its pure form occupies a very limited field above curve III which parallels the saturation curve. (The data from which this curve was constructed were taken from International Critical Tables (1928, Vol. 4, p. 228).) The 5-form, on the other hand is only stable at higher temperatures and its pure form occupies an extensive field bounded by curves V and VI.

Above curve VI and at temperatures higher than 45 to 50 °C, we pass, with increasing temperature, through the following fields: (1)  $5\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot x\text{H}_2\text{O} + \text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot x\text{H}_2\text{O}$ , (2)  $5\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot x\text{H}_2\text{O} + \text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot x\text{H}_2\text{O} + \text{Mg}(\text{OH})_2 \cdot 2\text{MgSO}_4 \cdot x\text{H}_2\text{O}$ , (3)  $\text{Mg}(\text{OH})_2 \cdot 2\text{MgSO}_4 \cdot x\text{H}_2\text{O}$ . This represents a decreasing ratio of  $\text{Mg}(\text{OH})_2 : \text{MgSO}_4$  in the reaction product with increasing temperature. Pure 1-form, like 3-form, occupies a very limited field above curve VII. Pure  $\frac{1}{2}$ -form, on the other hand occupies an extensive field to the right of curve IX. In the fields just discussed it has been difficult to draw the boundary curves with any great accuracy for two reasons. Firstly, the 1-form tends to occur in single crystals as does also  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and its lower hydrates and as has been pointed out the latter are difficult to remove by washing. Thus it is not always clear as to whether a sample contains a small amount of the 1-form or a hydrate of magnesium sulphate. Secondly, samples subjected to prolonged washing tend to hydrolyse and hence have a higher  $\text{Mg}(\text{OH})_2 : \text{MgSO}_4$  ratio than would be expected from the X-ray results. This effect is particularly marked for the samples in the upper right-hand corner of Figure 1.

The data set out in Figure 1 do not agree with those recorded by Delyon (1936) who found at 80° that below a concentration of 300 g/l of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  (equivalent to 15 per cent. of  $\text{MgSO}_4$ ) the precipitate was  $\text{Mg}(\text{OH})_2$  and above 500 g/l (24 per cent.  $\text{MgSO}_4$ )  $3\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 8\text{H}_2\text{O}$ . Under the latter conditions we would expect the 5-form. The reason for the difference is not clear but it should be noted that Walter-Lévy (1936*a*, 1936*b*) obtained the 3-form from chilled solutions, with which our results agree.

No data have been plotted in the extreme right-hand corner of Figure 1 since in this region, under normal atmospheric conditions, magnesium sulphate solutions of low concentrations boil. Figure 1 should terminate along a curve which represents the boiling point of magnesium sulphate solutions at various concentrations. This curve is not known with any accuracy and has not been plotted.

In separate experiments (with saturated solutions), it was established that the 5-form preceded the formation of either the 1-form or the  $\frac{1}{2}$ -form and this suggests that the forms lowest in  $\text{Mg}(\text{OH})_2$  crystallize by passing through the forms with higher  $\text{Mg}(\text{OH})_2$  content that can exist at the particular temperature being studied. A similar effect has been noted in the system  $\text{MgO}-\text{MgCl}_2-\text{H}_2\text{O}$  (Feitknecht and Held 1944; Demediuk, Cole, and Hueber 1955). However, this does not apply to the 3-form which appears without passing through the 5-form but can co-exist with it.

(b) *Some Properties of the Pure Phases*

In Figure 1, it has been indicated that four oxysulphates occur in the system  $\text{MgO-MgSO}_4\text{-H}_2\text{O}$  under the conditions studied and of these the 5-form and the 3-form have previously been described (Aspelund 1933; Delyon 1936; Walter-Lévy 1936*a*, 1936*b*) but the 1-form and the  $\frac{1}{2}$ -form appear to be new compounds. Consequently, the chemical and X-ray data on which the recognition of the four oxysulphate forms are based are recorded in Tables 1 and 2. Since in the results presented in Table 1, the  $\text{H}_2\text{O}$  was determined by difference,

TABLE 1  
CHEMICAL COMPOSITION OF PURE OXYSULPHATE PHASES

Com- position	Weight (%)	Molecular Propor- tions	No. of Molecules	Form	Conditions of Formation*	
					Temp. (°C)	Soln. Concn. (% w/v)
MgO	51.90	1.287	6.01	$5.0\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 3.0\text{H}_2\text{O}$	80	35
$\left\{ \begin{array}{l} \text{SO}_3^{++} \\ \text{H}_2\text{O}^{++} \end{array} \right.$	17.17	0.214	1			
	30.93	1.716	8.02			
MgO	37.05	0.919	4.10	$3.1\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 8.0\text{H}_2\text{O}$	30	Saturated
$\left\{ \begin{array}{l} \text{SO}_3^{++} \\ \text{H}_2\text{O}^{++} \end{array} \right.$	17.93	0.224	1			
	45.02	2.498	11.15			
MgO	30.15	0.748	2.01	$1.0\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 5.0\text{H}_2\text{O}$	80	Saturated
$\left\{ \begin{array}{l} \text{SO}_3^{++} \\ \text{H}_2\text{O}^{++} \end{array} \right.$	29.78	0.372	1			
	40.07	2.224	5.98			
MgO	34.28	0.850	1.50	$1.0\text{Mg}(\text{OH})_2 \cdot 2\text{MgSO}_4 \cdot 3.0\text{H}_2\text{O}$	110	Saturated
$\left\{ \begin{array}{l} \text{SO}_3^{++} \\ \text{H}_2\text{O}^{++} \end{array} \right.$	45.29	0.566	1			
	20.43	1.134	2.00			

\* Equilibrium conditions. Reaction between 1 g  $\text{MgO}$  and 100 ml of solution at concentration and temperature stated.

† By difference.

‡ The weight loss on ignition which includes  $\text{SO}_3 + \text{H}_2\text{O}$  has been determined separately as follows: 5-Form: Found 47.7%. Calc. 48.10%. 3-Form: Found 62.9%. Calc. 63.85%. 1-Form: Found 67.8%. Calc. 69.85%.  $\frac{1}{2}$ -Form: Found 69.4%. Calc. 65.72%.

a comparison has been made between the weight loss on ignition (which would include all the  $\text{H}_2\text{O}$  and most of the  $\text{SO}_3$ ) and the sum of  $\text{H}_2\text{O} + \text{SO}_3$  given by the chemical analyses. That the latter is slightly higher than the former, for all but the  $\frac{1}{2}$ -form, is an indication that the temperature of ignition was insufficient to decompose completely the  $\text{MgSO}_4$  part of the compounds. For the  $\frac{1}{2}$ -form the preparation must be slightly impure; it has already been indicated that it is very difficult to free this compound from small amounts of the 1-form and hydrates of magnesium sulphate.

TABLE 2

X-RAY DIFFRACTION POWDER PATTERNS OF PURE OXYSULPHATE PHASES\*

5·0Mg(OH) <sub>2</sub> ·MgSO <sub>4</sub> ·3·0H <sub>2</sub> O		3·1Mg(OH) <sub>2</sub> ·MgSO <sub>4</sub> ·8·0H <sub>2</sub> O		1·0Mg(OH) <sub>2</sub> ·MgSO <sub>4</sub> ·5·0H <sub>2</sub> O		1·0Mg(OH) <sub>2</sub> ·2MgSO <sub>4</sub> ·3·0H <sub>2</sub> O	
<i>I</i> †	<i>d</i> (kX)	<i>I</i>	<i>d</i> (kX)	<i>I</i>	<i>d</i> (kX)	<i>I</i>	<i>d</i> (kX)
vw	7·77	mw	10·07	m	9·01	vvw	8·05
m	6·88	mw	5·78	mw	7·73	m	7·22
vw	6·11	m	5·40	vw	6·92	mw	6·37
vw	5·70	w	5·03	w	6·14	m	5·78
s	5·13	ms	4·72	w	5·79	mw	5·32
?	4·76	mw	4·34	m	5·42	m	4·80
w	4·30	vvw	4·20	m	4·83	vw	4·62
ms	3·87	w	3·96	mw	4·54	mw	4·28
vw	3·62	w	3·73	w	4·32	mw	4·07
w	3·42	vw	3·53	w	4·09	mw	3·89
vw	3·30	vw	3·27	mw	3·95	w	3·59
w	3·07	mw	3·08	w	3·62	mw	3·41
m	2·97	w	2·99	vw	3·51	mw	3·21
vw	2·87	vw	2·94	w	3·31	vw	3·08
mw	2·78	w	2·87	w	3·19	ms	2·97
md	2·61	vw	2·81	vw	3·07	vw	2·90
w	2·461	w	2·68	w	2·96	mw	2·80
vw	2·381	w	2·63	w	2·85	mw	2·66
s	2·248	ms	2·53	mw	2·68	vw	2·58
w	2·083	m	2·456	w	2·59	mw	2·497
mb	2·001	mw	2·381	w	2·51	mw	2·385
vw	1·934	vw	2·275	w	2·410	mw	2·313
mw	1·884	vw	2·185	mw	2·290	vvw	2·254
w	1·823	vw	2·109	w	2·218	vvw	2·183
mw	1·759	mw	1·998	w	2·148	w	2·108
m	1·701	mw	1·958	w	2·077	m	2·029
mw	1·662	mw	1·892	mw	2·001	w	1·997
m	1·606	vw	1·791	mw	1·946	mw	1·919
w	1·572	w	1·760	vw	1·895	w	1·870
m	1·548	vw	1·680	vw	1·826	vvw	1·856
m	1·509	vw	1·652	w	1·751	vvw	1·747
		vw	1·617	w	1·682	mw	1·701
		mw	1·573	mw	1·650	w	1·646
		mw	1·550	vw	1·605	rw	1·621
		w	1·532	w	1·552	mw	1·587
				w	1·516	w	1·518

\* Lines not listed below 1·500 kX.

† Intensity scale: s, strong; ms, medium strong; m, medium; mw, medium weak; w, weak; vw, very weak; vvw, very very weak; ?, presence uncertain; d, diffuse; b, broad.

The number of water molecules for a particular oxysulphate compound varies with the preparation, being dependent on the time of washing and the quantity and temperature of the methanol used. Preparations of the 5-form made below 100 °C contain mostly three molecules of water but at higher

temperatures two water molecules only are present; these results agree with those of Walter-Lévy (1936b). However, the X-ray powder patterns of these preparations with three and two molecules of water are very similar (if not identical) and it may be that for the 5-form two molecules of water only are essential to the structure. For the 3-form the number of water molecules in different preparations ranges from 4 to 13, but 8 as reported earlier by Delyon (1936) and Walter-Lévy (1936a, 1936b) seems to be essential to the structure. Of the other phases the 1-form has five and the  $\frac{1}{2}$ -form three molecules of water. A detailed study of the number of water molecules in oxysulphate compounds is being made and the results will be reported separately.

The oxysulphates are much more stable than the oxychlorides previously described (Cole and Demediuk 1955; Demediuk, Cole, and Hueber 1955). No change in composition was detected in any form after samples had been exposed to an atmosphere of  $\text{CO}_2$  at 35 per cent. relative humidity for 3 months. They are also stable when left in contact with their original solutions at any temperature below that at which they were formed or when left in the atmosphere.

#### IV. CONCLUSIONS

This examination by chemical and X-ray methods of the compounds formed in the system  $\text{MgO-MgSO}_4\text{-H}_2\text{O}$  has confirmed the existence of the two magnesium oxysulphates  $5\text{Mg}(\text{OH})_2\cdot\text{MgSO}_4\cdot 3\text{ or } 2\text{H}_2\text{O}$  and  $3\text{Mg}(\text{OH})_2\cdot\text{MgSO}_4\cdot 8\text{H}_2\text{O}$  reported by earlier workers, and has shown the existence of two more forms of the composition  $\text{Mg}(\text{OH})_2\cdot\text{MgSO}_4\cdot 5\text{H}_2\text{O}$  and  $\text{Mg}(\text{OH})_2\cdot 2\text{MgSO}_4\cdot 3\text{H}_2\text{O}$ . (An equilibrium diagram has been prepared showing the phases formed in  $\text{MgSO}_4$  solutions up to saturation and temperatures from 30 to 120 °C.) The 3-form occurs at low temperatures, the 5-form at both low and high temperatures, the 1-form at intermediate temperatures and high concentrations, and the  $\frac{1}{2}$ -form at high temperatures and high concentrations.

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## A NEW INTERPRETATION OF THE ACIDIC AND BASIC STRUCTURES IN CARBONS

### I. LACTONE GROUPS OF THE ORDINARY AND FLUORESCEIN TYPES IN CARBONS

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#### Summary

Methylation of a sugar carbon or carbon black with diazomethane produces a methoxyl group which is readily hydrolysed by dilute acid but which is not due to the presence of a simple carboxylic ester, since the titration curves of the carbons are those of much weaker acids. It most probably arises from the methylation of a lactone which is present in conjunction with a phenol, such as occurs in the fluorescein and phthalein dyestuffs. This, however, accounts for only part of the acidity of the carbons, some of which is due to a group which reacts with alkali but not with diazomethane and is probably a normal lactone group. The remainder of the acidity of the carbons is due to phenolic hydroxyl groups. Infra-red spectroscopic evidence is presented in support of these views. The effects of temperature and of oxidation on the concentration of these various groups have also been studied.

#### I. INTRODUCTION

In 1929, Krulyt and de Kadt first reported the adsorption of alkali on sugar carbons which had been heated to low temperatures (L-carbons), and Schilow and Tschmutow (1929) suggested that this adsorption was due to the presence of an acidic oxide on the surface of the carbon. Bartell and Miller (1922) had earlier studied the adsorption of acids on sugar carbons activated at high temperatures (H-carbons). Burstein and Frumkin (1929) first showed that a carbon outgassed at 1000 °C and cooled in a vacuum did not adsorb electrolytes unless molecular oxygen was admitted. Over the following years Frumkin's school evolved an electrochemical theory to account for the adsorption of acids and alkalis on H-carbons, which were regarded as behaving as oxygen and hydrogen electrodes. Steenberg (1944) proposed an explanation for the pH changes which accompany the adsorption of organic electrolytes on carbon. An L-carbon was regarded as a cation-exchange adsorbent, but a physical mechanism was suggested for the adsorption of inorganic acids on H-carbons. Steenberg's theory did not account for the observations of Frumkin and others on the effect of molecular oxygen on the adsorption of acids by H-carbons.

It is the purpose of the present series of papers to provide a more consistent explanation of these observations and to suggest the presence, on the surface of various carbons, of reactive groups which are responsible for the adsorption of alkali and with whose properties all the experimental data are consistent.

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It is well established that activated carbons and carbon blacks possess acidic or non-acidic surfaces depending on the nature of their prior heat-treatment. What has been termed "alkali adsorption" in the earlier literature is the amount of alkali metal ion exchanged for hydrogen ion by the neutralization of surface acids, and is not due to molecular adsorption of the alkali molecule. It is therefore markedly dependent on the pH value of the solution when adsorption equilibrium is reached. The subject has been recently discussed by Garten and Weiss (1955), and it was suggested that the activity arises from the presence of phenolic groups, since the shape of the titration curve resembles that of an acid of a strength similar to a phenol. Similar curves were also obtained by Villars (1947) for a series of carbon blacks. Hofmann and Ohlerich (1950) observed that sugar carbons can be methylated with diazomethane and that the methoxyl content of the products decreases after boiling with N acid. Studebaker *et al.* (1956) observed a similar behaviour with carbon blacks, and concluded that the non-hydrolysable fraction arises from methylation of a phenol and the hydrolysable fraction from methylation of a carboxyl group. Comparison of the titration curves for carbons and the titration curves of Griessbach (1939) for resins containing phenol groups with and without carboxylic acid groups shows that normal arylcarboxylic acid groups, if present on the surface of the carbons, should have been detected. No adequate explanation has been advanced to account for the methylation experiments, which at first sight suggest the presence of carboxylic groups, and the titration curves which suggest the presence of a weaker acid.

New experimental results to be presented in this paper show yet another contradiction of the former conclusions, since usually the total acidity of a carbon, as measured by the amount of alkali adsorbed, is considerably greater than that accounted for by the total methoxyl content of the methylated carbon. This result suggests the presence of a group which is not methylated with diazomethane but which reacts with alkali.

"Carbolac 1", an ink black, was chosen for this study because of its exceptionally high acidity, its freedom from ash, and because it was the only carbon black sufficiently transparent to give a useful infra-red spectrum. The black was heated in nitrogen at various temperatures between 400 and 800 °C. The effect of oxidation was studied on samples prepared by reheating in air the black which had been heated in nitrogen to 800 °C. The results are compared with those of Studebaker *et al.* (loc. cit.) who studied a series of commercial carbon blacks. A series of sugar carbons was prepared by heating a sugar char in air over the same range of temperature. The 800 °C carbon was reoxidized by heating it in air at temperatures between 400 and 800 °C.

Garten, Eppinger, and Weiss (1956) showed that the surface area of an ink black changed only slightly on heating the black in nitrogen between 400 and 800 °C. The experimental results on "Carbolac 1" may therefore be expressed either as concentration of active groups per unit weight or as concen-

tration per unit surface area. There is good reason to believe\* that the results for sugar carbons should be expressed as concentrations per unit weight, and we shall therefore use this method throughout.

Where possible the investigation has been supplemented by an infra-red study, but useful spectra of less acidic ink blacks or of channel blacks could not be obtained. It is known that sugar carbons become opaque to infra-red radiation on heating above 600 °C (Kmetko 1951).

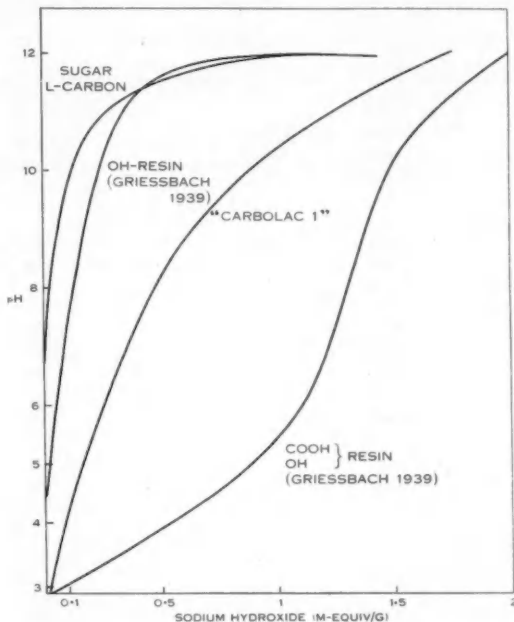


Fig. 1.—The titration curves of "Carbolac 1" and a sugar carbon activated at 400 °C are compared with those of formaldehyde condensation resins containing phenolic, and phenolic and carboxylic groups respectively.

## II. PHENOLIC HYDROXYL GROUPS

The titration curves of "Carbolac 1" and of the sugar carbons activated at 400 °C are shown in Figure 1 and are similar to those previously reported (Villars 1947; Garten and Weiss 1955). They are comparable with the curve obtained

\* Surface area measurements on a series of sugar carbons by the B.E.T. method (Garten and Weiss loc. cit.) show that a carbon activated at 550 °C has the same area as one activated at 800 °C but 10 times that of a carbon activated at 400 °C. The anomalously low value for the apparent surface area of the 400 °C carbon causes the alkali uptake, calculated on the basis of the measured surface area, to appear unreasonably high. A similar behaviour was found with an ion-exchange resin of the phenol-formaldehyde type, whose porosity probably resembles that of a low-temperature sugar carbon.

by Griessbach for a phenolic resin. The ion-exchange capacity of "Carbolac 1" is much greater than that of the phenolic resin, and this accounts for the difference in slope between the two curves.

In Tables 1, 2, and 3 are shown the methoxyl contents of the series of carbon blacks and sugar carbons after methylation with an ethereal solution of diazomethane and after hydrolysis of the resultant methylated carbon with N acid. It is reasonable to suppose that the methoxyl groups which resist hydrolysis are the methyl ethers of ordinary phenols or of weakly acidic enols,

TABLE 1  
EFFECT OF TEMPERATURE AND OXIDATION ON THE ACIDIC PROPERTIES OF "CARBOLAC 1"

Treatment	NaOH Adsorption ( $\mu$ -equiv/g)	Total —CH <sub>3</sub> O ( $\mu$ -equiv/g)	Phenol* ( $\mu$ -equiv/g)	f-Lactone† ( $\mu$ -equiv/g)	n-Lactone‡ ( $\mu$ -equiv/g)
"Carbolac 1", original:					
Batch 1 .. ..	1880	1460	560	900	420
Batch 2 .. ..	1800	1400	520	880	400
"Carbolac 1" (batch 1) heated in N <sub>2</sub> at:					
400 °C .. ..	1740	1380	450	930	360
500 °C .. ..	1540	1220	520	700	320
600 °C .. ..	1060	810	320	490	250
700 °C .. ..	610	580	120	460	30
800 °C .. ..	430	420	80	340	10
"Carbolac 1" (batch 2) heated in N <sub>2</sub> at:					
800 °C .. ..	230	250	70	180	—20
"Carbolac 1" (batch 2) heated in N <sub>2</sub> at 800 °C and reoxidized in air at:					
400 °C .. ..	590	390	170	220	200
500 °C .. ..	520	330	160	170	190
600 °C .. ..	400	260	80	180	140
700 °C .. ..	290	150	50	100	140

\* Phenol = non-hydrolysable methoxyl.

† f-Lactone = total methoxyl minus phenol.

‡ n-Lactone = NaOH adsorption minus total methoxyl.

since the ease of hydrolysis of an ether decreases markedly with decrease in the acidic strength of the parent enol (Fuson 1950), and for convenience the term "phenol" will be used to cover both types of group. The phenolic concentrations given in Tables 1–3 are thus identical with the methoxyl concentrations after hydrolysis with acid.

Phenolic groups account for a small part of the acidity of "Carbolac 1" and their concentration falls steadily with increase of temperature (Table 1). When "Carbolac 1" which has been heated to 800 °C is reoxidized in air at

400 °C the phenolic content increases but does not reach the original value. Table 2 shows that phenolic groups account for only about one-tenth of the acidity of the 400 °C sugar carbon, but that their concentration is not appreciably affected by heating in air to higher temperatures or by reoxidizing the 800 °C carbon at lower temperatures. Table 3 shows that phenolic groups are present to a smaller extent in channel blacks than in ink blacks. Our former conclusion that the acidity of ink blacks and sugar L-carbons arises solely from ordinary phenolic groups is inconsistent with the new experimental data presented above.

A carbonyl group chelated to a phenolic hydroxyl group has been suggested by Brown (1955) as a possible explanation for the strong absorption band at 1600  $\text{cm}^{-1}$ , which is always observed in the spectra of coals and is also present

TABLE 2  
EFFECT OF TEMPERATURE AND OXIDATION ON THE ACIDIC PROPERTIES OF SUGAR CHAR

Treatment	NaOH Adsorption ( $\mu\text{-equiv/g}$ )	Total —CH <sub>3</sub> O ( $\mu\text{-equiv/g}$ )	Phenol ( $\mu\text{-equiv/g}$ )	f-Lactone ( $\mu\text{-equiv/g}$ )	n-Lactone ( $\mu\text{-equiv/g}$ )
Sugar char, heated in air to :					
400 °C .. ..	590	110	60	50	480
500 °C .. ..	220	90	40	50	130
600 °C .. ..	140	20	10	10	120
700 °C .. ..	140	90	40	50	50
800 °C .. ..	130	80	20	60	50
Sugar char, heated in air to 800 °C and re- oxidized in air at :					
400 °C .. ..	320	150	50	100	170
500 °C .. ..	270	150	40	110	120
600 °C .. ..	220	150	40	110	70
700 °C .. ..	180	150	30	120	30

in that of "Carbolac 1" (see Section IV). A chelated phenolic hydroxyl group would not react with dilute aqueous alkali, or with ethereal diazomethane (Schonberg and Mustafa 1946), and would not therefore be detected in the above experiments.

Since these acidic carbons reduce silver nitrate, it is possible that some of the phenol groups may function as hydroquinones, as suggested by Garten and Weiss (1955).

### III. LACTONES

#### (a) Lactones That can be Methylated

The results in Tables 1, 2, and 3 show the presence of a group, in considerable concentrations in some carbons, which can be methylated by an ethereal solution of diazomethane to give a product which can be hydrolysed by dilute acid. It has an acid strength similar to that of a phenol rather than that of a carboxylic

TABLE 3  
ACIDIC PROPERTIES OF COMMERCIAL INK AND CHANNEL BLACKS\*

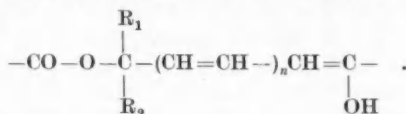
Inks and Blacks	B.E.T. <sup>†</sup> Surface Areas (sq. m/g)	Electron <sup>†</sup> Microscope Surface Areas (sq. m/g)	NaOH Adsorption ( $\mu$ -equiv/g)	Total —CH <sub>3</sub> O ( $\mu$ -equiv/g)	Phenol <sup>‡</sup> ( $\mu$ -equiv/g)	f-Lactone ( $\mu$ -equiv/g)	n-Lactone ( $\mu$ -equiv/g)
"Carbolac 1" (batch 1; high colour ink black) ..	1000	264	1880	1460	560	900	420
"Mogul A" (long flow ink black)	293	82	1180	542	210	332	638
"Elf 0" (low colour ink black)	161	94	580	245	103	142	335
"Spheron 3" (hard processing channel black) ..	—	—	400	155	65	90	245
"Spheron 6" (medium pro- cessing channel black) ..	120	106	370	142	55	87	228
"Spheron 9" (easy processing channel black) ..	100	94	460	97	48	49	363

\* Products of Messrs. Godfrey L. Cabot Inc., U.S.A.

<sup>†</sup> Data from "Cabot Carbon Blacks under the Electron Microscope," Vol. 2, No. 10, October 1950.

<sup>‡</sup> Results reported by Studebaker *et al.* (loc. cit.).

acid.\* It is suggested that the group is a lactone of the type present in the fluorescein or phenolphthalein dyestuffs, which behaves as a weak acid, and, unlike the simple lactones, can be methylated with diazomethane to give an ester which can be hydrolysed with dilute acid. Such a group could be attached to the edge of a layer plane of the carbon as shown in Figure 2, which represents one example of the many possible structures of the type:



The fluorescein and phthalein lactones behave as acids of a strength comparable with that of phenol: phenolphthalein, for example, has a dissociation constant of  $1.15 \times 10^{-9}$  (Kolthoff 1931). Fluorescein can be methylated with diazomethane to give the ester of the monomethyl ether, which is readily hydrolysed by dilute acid (Fischer and Hepp 1913). Phenolphthalein and fluorescein can be considered as tautomeric mixtures of the lactone and quinone structures analogous to Ia and Ib (Fig. 2), but a recent infra-red spectroscopic study by Davies and Jones (1954) has shown that they exist predominantly in the lactone form. On reaction with alkali the lactone ring opens to give a quinonoid structure III, and a similar quinonoid structure II results on methylation. The infra-red spectra discussed in Section IV are consistent with the idea that the carbons contain lactone groups which undergo similar reactions to these.

The change in magnetic susceptibility of the carbons on treatment with alkali is consistent with the occurrence of a change to a quinonoid structure of the type postulated above. The diamagnetic susceptibility of "Carbolac 1" is reduced from  $-1.82$  to  $-0.87 \times 10^{-6}$  on treatment with 20 per cent. aqueous alcoholic potash, and that of "Elf 0" ink black from  $-1.25$  to  $-0.96 \times 10^{-6}$ . Simple salt formation cannot account for this change but it can be explained by the replacement of some aromatic bonds, which have diamagnetic increments, by quinonoid bonds, which have paramagnetic increments. Part, however, of the observed decrease in diamagnetic susceptibility may perhaps be accounted for by oxidation of hydroquinones by molecular oxygen during the hydrolysis.

Although the only examples known to us of lactones with the properties just described are  $\gamma$ -lactones, there does not seem to be any reason why analogous  $\delta$ -lactones should not behave similarly, and for convenience both  $\gamma$ - and  $\delta$ -lactones of this type will be designated as "f-lactones", that is, "fluorescein type lactones". The infra-red spectrum of "Carbolac 1" is consistent with the presence of lactones and favours  $\gamma$ -lactones.

As shown in Table 1 this group accounts for about half the total acidity of "Carbolac 1", and is stable to about  $400^\circ\text{C}$ , above which its concentration steadily decreases with temperature. Fluorescein decomposes in the molten

\* The presence of concentrations of carboxylic acid groups too small to be detected in the titration curves cannot be excluded.

state at approximately 350 °C with the evolution of carbon dioxide, while an f-lactone group on the carbon surface may be expected to decompose to a quinone as shown in Figure 2. It thus appears that f-lactone groups on the carbon surface are more stable than in fluorescein. Their concentration in "Carbolac 1" is slightly increased by heating to 800 °C followed by reoxidation on heating in air to 400 °C, but decreased when the temperature of reoxidation is increased to 700 °C. Table 3 shows that ink blacks in general contain a higher concentration of this group than do channel blacks.

The presence of f-lactone groups accounts for only about one-tenth of the acidity of 400 °C sugar carbon (Table 2). The concentration of the group increases when the 800 °C carbon is reoxidized at 400 °C and remains constant when the temperature of oxidation is increased. The concentration of the

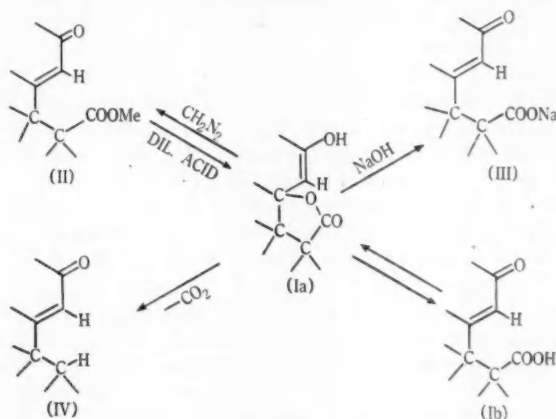


Fig. 2.—The reactions of an f-lactone.

group is such that its variation is just within the limits of experimental error, so that it is not possible to draw any valid conclusions concerning the manner in which its concentration varies with temperature. This low concentration renders infra-red and magnetic measurements ineffective as a means of detecting f-lactone groups in sugar carbons, and our conclusions concerning their presence are therefore based entirely on the behaviour of these carbons, which is similar to that of "Carbolac 1", towards diazomethane and hydrolysis of the methylated products.

#### (b) Lactones That cannot be Methylated

The data in Tables 1, 2, and 3 show that for many of the carbons the total acidity, calculated from the alkali adsorption, is much greater than that derived from the total methoxyl content of the methylated carbons. This indicates the presence of an acid group which is not methylated by diazomethane. As mentioned earlier, the tenfold increase in the B.E.T. surface area of the sugar carbons when the temperature of activation is raised from 400 to 500 °C indicates



a marked change in the ability of the carbon to absorb nitrogen, but there is no change in the total methoxyl content of the corresponding methylated carbons. We therefore consider it unlikely that differences in porosity can account for the discrepancy between the alkali uptake and the methoxyl content.

Table 3 shows a considerable difference between the alkali adsorption of channel blacks and the total methoxyl content of their methylated products. The surface areas of the channel blacks "Spheron 6" and "Spheron 9" are similar when measured by the B.E.T. method and by electron microscopy, which indicates that these materials are essentially non-porous. It is unlikely therefore that the large discrepancy between the alkali adsorption and the total methoxyl content in these two carbons can be accounted for by a difference in accessibility towards alkali and diazomethane. The large discrepancies also observed with the more porous ink and sugar carbons are probably not due to porosity differences either.

The most plausible explanation for the discrepancy between the alkali adsorption and the total methoxyl content is that it is due to the presence of normal lactones which are probably  $\delta$ -lactones, since these are more readily hydrolysed by cold alkali than  $\gamma$ -lactones. For convenience we shall term these groups "n-lactones". On hydrolysis 1 or 2 moles of alkali will be consumed per mole of lactone, depending on whether an alcoholic or phenolic hydroxyl group is formed on opening the lactone ring. The n-lactone concentrations presented in Tables 1-3 are calculated on the basis of 1 mole of alkali consumed per mole of lactone.

The n-lactone group accounts for only a minor part of the acidity of "Carbolac 1", and its concentration decreases with increase in the temperature of treatment (Table 1), but it occurs to a considerable extent in some of the other carbon blacks, and particularly in the ink black "Mogul A" (Table 3). Re-oxidation at 400 °C of "Carbolac 1" which has been heated in nitrogen at 800 °C markedly increases the concentration of this group, but the concentration decreases when the oxidation is carried out at higher temperatures.

The greater part of the acidity of the 400 °C sugar carbon may be attributed to the presence of this lactone grouping (Table 2). The concentration of the group decreases when the temperature of activation is increased, but reappears when the 800 °C carbon is reoxidized at 400 °C.

#### IV. INFRA-RED SPECTROSCOPIC DATA

It is difficult to obtain good infra-red spectra of carbon samples on account of the high loss of light by scattering which is particularly noticeable in the high-frequency region. In addition to this loss of light there is the high level of continuous background absorption which has been observed by previous workers in the spectra of high-rank coals (Brown 1955). We have not been able to obtain reliable measurements of absorption in the 3000-3600  $\text{cm}^{-1}$  region, and have confined our observations to the 1500-2000  $\text{cm}^{-1}$  region.

The interpretation of the spectra is rendered difficult for the following reasons. In carbon blacks similar functional groups, for example, lactone

groups, may form part of a wide variety of different chemical structures in a given carbon particle, so that the absorption bands observed are broader than those found in simple molecules. Nor is it known whether such functional groups exist as independent, non-associated structures, when their absorption should be compared with measurements on simple compounds in the vapour phase or in dilute solution, or whether association occurs between groups on the same or adjacent layer planes, in which case it would be better to compare their absorption with that of simple compounds in the solid state. There is some reason to believe that free-radical structures occur in carbons and are connected with their semiconductivity (Mrozowski 1952*a*, 1952*b*), but it is not known how these structures, if they exist, will influence the infra-red spectra of the carbons. If the semiconductivity of a carbon black arises from loss of hydrogen atoms from its structure, as suggested by Mrozowski (*loc. cit.*), it might be expected that the infra-red absorption would be influenced in the same way as it is in simple molecules by the substitution of an electronegative atom or group. However, since the evidence presented in Section II suggests the presence in "Carbolac 1" of phenolic groups with dissociation constants not greatly different from those of ordinary phenols it seems unlikely that the postulated free-radical structures would greatly influence the infra-red absorption frequencies due to the presence of carbonyl groups.

The infra-red spectra of the various carbons are shown in Figures 3 and 4. The spectrum of "Carbolac 1" shows absorption bands at 1600 and 1760  $\text{cm}^{-1}$ .

The origin of the 1600  $\text{cm}^{-1}$  band, which occurs in coals and other carbonaceous materials, has been the subject of much discussion. It may be due to vibrations of the aromatic  $\text{C}=\text{C}$  bonds or of carbonyl groups chelated to phenolic hydroxyl groups (Brown 1955; Friedel and Queiser 1956). The 1760  $\text{cm}^{-1}$  band undoubtedly arises from the presence of a carbonyl group, which may be that of a lactone (Bellamy 1954). It is not possible to decide from the infra-red evidence whether the lactone is  $\gamma$ - or  $\delta$ -, saturated or unsaturated. The high frequency of the band perhaps favours the presence of a  $\gamma$ - rather than a  $\delta$ -lactone. It is seen from Figure 3 that the intensity of this band relative to that of the 1600  $\text{cm}^{-1}$  band does not appreciably diminish until "Carbolac 1" has been heated to 600  $^{\circ}\text{C}$ . This behaviour confirms our belief that the 1760  $\text{cm}^{-1}$  band is connected with the f-lactone group. Above 600–700  $^{\circ}\text{C}$  the intensity of the 1600  $\text{cm}^{-1}$  band begins to diminish also.

The spectrum of the sodium salt of "Carbolac 1" is shown in Figure 3. The disappearance of the 1760  $\text{cm}^{-1}$  band in this spectrum confirms the view that the group responsible for this band in the spectrum of "Carbolac 1" is connected with the adsorption of alkali. The 1600  $\text{cm}^{-1}$  band of "Carbolac 1" shifts to 1590  $\text{cm}^{-1}$  in the sodium salt and is broadened. This behaviour is consistent with the production of a carboxylate ion, having an absorption band in the region 1550–1610  $\text{cm}^{-1}$  (Bellamy *loc. cit.*) which, superimposed on the 1600  $\text{cm}^{-1}$  band, would produce the effect observed. According to the reaction scheme shown in Figure 2 the production of quinone groups is to be expected on hydrolysis of f-lactone groups. However, Davies and Jones (*loc. cit.*) did not

observe in the spectra of the sodium salts of fluorescein and phenolphthalein the expected quinone carbonyl frequency near  $1680\text{ cm}^{-1}$ , nor any other strong absorption bands that could be assigned to this group. No absorption band near  $1680\text{ cm}^{-1}$  is found in the spectrum of the sodium salt of "Carbolac 1",

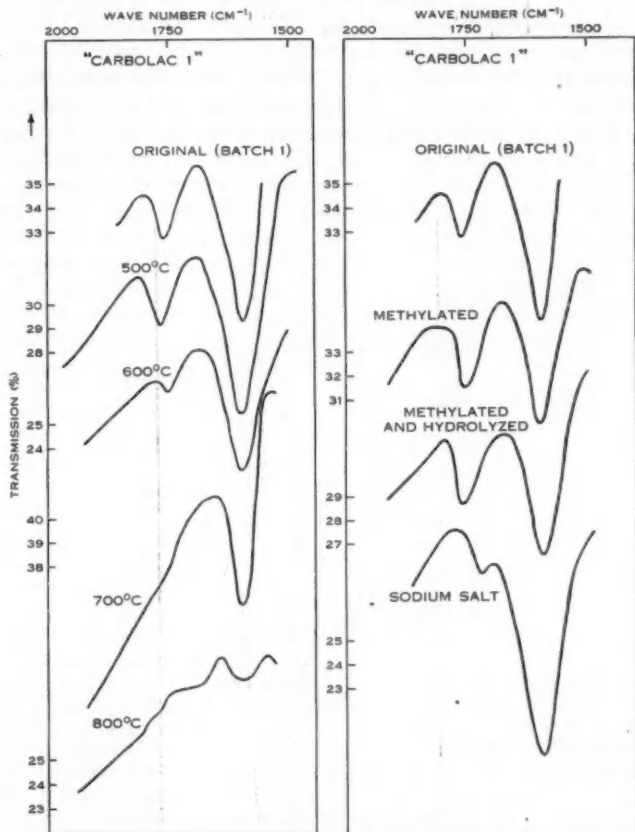
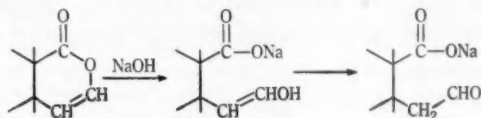


Fig. 3.—Infra-red spectra of "Carbolac 1" and a series of derivatives prepared by heat-treatment and reactions with diazomethane and alkali.

but the weak band near  $1720\text{ cm}^{-1}$  suggests the presence of an aldehyde or ketone group, which may arise from the hydrolysis of an  $\alpha$ -lactone. Such groups arise during the hydrolysis of an unsaturated lactone if a vinyl alcohol structure results from the hydrolysis and rearranges to the more stable ketone or aldehyde. For example, 5,6,7-trimethylisocoumarin gives  $\omega$ -hydroxy-2,3,4-

trimethoxy-6-carboxystyrene (Tschitschibabin *et al.* 1929). This reaction is of the general type:



The spectrum of "Carbolac 1" after methylation with diazomethane (Fig. 3) shows that the relative intensities of the 1600 and 1760  $\text{cm}^{-1}$  bands have changed. A similar behaviour was observed by Ceh and Hadzi (1956)

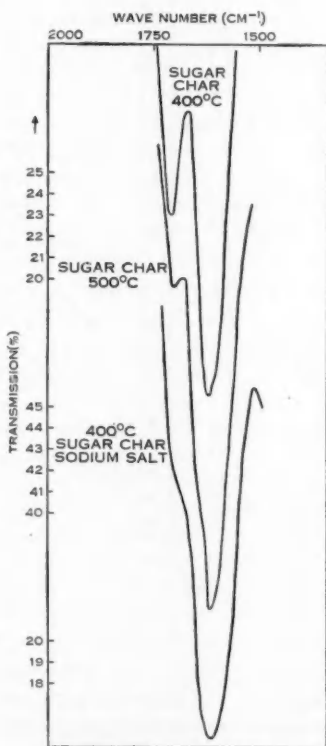


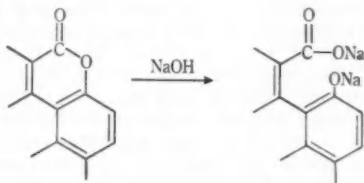
Fig. 4.—Infra-red spectra of a series of sugar carbons.

on methylating a series of humic acids. It is not possible to decide which band has changed in absolute intensity. If it is assumed to be the 1760  $\text{cm}^{-1}$  band, the increase of the intensity may be due to the conversion of a lactone into an

ester, though this frequency is high for an ester unless the group is present in a non-associated form (Hartwell, Richards, and Thompson 1948).

The infra-red spectrum of sugar carbon activated at 400 °C shows strong absorption bands in the neighbourhood of 1625 and 1705  $\text{cm}^{-1}$  and is similar to that reported for a sugar carbon by Friedel and Queiser (*loc. cit.*). The 1705  $\text{cm}^{-1}$  band is consistent with the presence of a carbonyl group, which may be that of an unsaturated  $\delta$ -lactone. An unsaturated  $\delta$ -lactone absorbing in this region has been reported by Govindachari, Nagarajar, and Pai (1956). When the carbon is activated at 500 °C the intensity of the band falls, and this parallels the decrease in concentration of  $\delta$ -lactone groups shown in Table 2.

The spectrum of the sodium salt of the 400 °C sugar carbon is shown in Figure 4. The 1625  $\text{cm}^{-1}$  band has moved to 1610  $\text{cm}^{-1}$  and has broadened, which is consistent with the superposition of an absorption band due to a carboxylate ion. The loss of the 1705  $\text{cm}^{-1}$  band confirms the idea that the presence of this band in the sugar carbon is connected with at least some of the acidic properties of the carbon. The almost complete lack of a band above 1700  $\text{cm}^{-1}$  in the sodium salt of sugar carbon suggests that in contrast with "Carbolac 1" a non-vinyl hydroxyl group has been formed on hydrolysis, which is certainly the case with the unsaturated  $\delta$ -lactone described by Govindachari, Nagarajar, and Pai (*loc. cit.*):



## V. EXPERIMENTAL

The detailed experimental methods follow.

(i) *Preparation of the Carbons.*—"Carbolac 1" was heated at temperatures ranging from 400–800 °C in a slow stream of dry pure nitrogen. The nitrogen, initially containing <10 p.p.m. oxygen, was passed over copper at 400 °C before entering the furnace. The carbon was retained at the desired temperature for a period of 2 hr and then cooled in the nitrogen. A further series of carbons was prepared from "Carbolac 1" which had been heated to 800 °C by reheating it in air for 2 hr at various temperatures between 400 and 800 °C. The carbons were cooled in an atmosphere of pure nitrogen.

Sugar char was activated at temperatures between 400 and 800 °C according to the method previously described (Garten and Weiss *loc. cit.*). The 800 °C char was reoxidized in air as was "Carbolac 1". All carbons were stored in an atmosphere of nitrogen.

(ii) *Alkali Adsorption.*—Carbon (0.500 g) was added to a 0.05N sodium hydroxide solution (40 ml) and shaken for 2 days, filtered, and the filtrate titrated with standard acid using bromothymol blue as the indicator. To flocculate the colloidal suspensions of "Carbolac 1" a saturated sodium chloride solution (5 ml) was added before the filtration.

(iii) *Methylation.*—The methylation of the carbons with ethereal diazomethane and the hydrolysis of the methylated carbons with N hydrochloric acid were performed as described by Hofmann and Ohlerich (*loc. cit.*) and by Studebaker *et al.* (*loc. cit.*). The methoxyl content of the methylated carbons was determined by the standard method of Vieboeck and Brecher on the microscale.

(iv) *Potentiometric Titration*.—A potentiometric titration of "Carbolac 1" was performed in the manner described in an earlier paper (Garten and Weiss loc. cit.).

(v) *Spectroscopic Technique*.—The infra-red spectra were measured with a Perkin-Elmer model 12 C spectrometer, converted to a double-pass instrument, and using a sodium chloride prism. The specimens were measured as mulls in "Nujol". "Carbolac 1" and its derivatives were already sufficiently finely divided, but the sugar carbons were dry-ground in a stainless steel ball-mill for 2 days before mulling with "Nujol". All specimens were dried *in vacuo* over phosphorus pentoxide for at least 24 hr and then measured as rapidly as possible. Optimum resolution of the absorption bands was obtained by adjusting the sample thickness until the general transmission level in the 1500–1800  $\text{cm}^{-1}$  region was 20–40 per cent. A reference spectrum of "Nujol" alone was run immediately after measuring each sample, using the same slit-width but altering the amplifier gain to give roughly the same signal as for the specimen. The spectrum was plotted by a point-by-point measurement of the ratio of the signals obtained in the two measurements. The absorption frequencies are quoted to the nearest 5  $\text{cm}^{-1}$ , which is regarded as the limit of accuracy obtainable in this type of measurement.

## VI. ACKNOWLEDGMENTS

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# A NEW INTERPRETATION OF THE ACIDIC AND BASIC STRUCTURES IN CARBONS

## II. THE CHROMENE-CARBONIUM ION COUPLE IN CARBON

By V. A. GARTEN\* and D. E. WEISS\*

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### Summary

The conflicting views of Frumkin, Shilov, and Steenberg on the chemical and adsorptive behaviour of sugar carbons activated at 800 °C (H-carbons) can be reconciled by postulating that the carbons contain chromene structures. The same is true of certain carbon blacks. The chromene system is readily oxidized at room temperature in the presence of acid to the corresponding benzopyrylium (carbonium) system, with the adsorption of the anion of the acid and the liberation of hydrogen peroxide. This reaction accounts for the dependence on the partial pressure of oxygen of adsorption of acid from dilute solutions, for the formation of peroxide from carbon with acids, and for the linear relationship between the potential of an H-carbon electrode and pH. A theoretical interpretation of the electrochemical behaviour of the chromene-carbonium ion couple is in good quantitative agreement with the observed behaviour of a cathodically polarized carbon electrode in acid solution. The ability of H-carbons to catalyse the oxidation of ferrous iron by molecular oxygen can also be accounted for by this couple, the concept of which is in agreement with the observed kinetic behaviour of the reaction.

### I. INTRODUCTION

Sugar carbons activated in oxygen or air at low temperatures, *c.* 400 °C— and named L-carbons by Steenberg (1944)—adsorb alkali but only very little mineral acid. However, activation at 800 °C produces carbons named H-carbons, which adsorb acid but not alkali. It has been shown in a previous paper (Garten and Weiss 1955) that carbon blacks behave analogously. The factors responsible for acid adsorption have been the subject of considerable discussion since 1927. One school maintains that the adsorption is an electrochemical process, another that it is due to neutralization of surface oxides of basic character, while a third believes that it is purely physical adsorption. Convincing arguments have been advanced in support of each of these apparently conflicting points of view. It is the purpose of the present paper to put forward a different hypothesis, which in the light of present knowledge can satisfactorily reconcile the experimental facts on which the three earlier proposals were based.

Burstein and Frumkin (1929) first showed that carbons outgassed at 950 °C did not adsorb mineral acid from a dilute solution but did so when oxygen was admitted to a suspension of the carbon in the acid. Shilov and Chmutov (1930) then showed that the adsorption was dependent on the oxygen pressure

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in the system, provided it did not exceed about 20 mm Hg. Some acid was still adsorbed by their outgassed carbon in the absence of oxygen, but this was shown by Frumkin, Burstein, and Lewin (1931) to be due to traces of oxygen which could be removed completely only if the carbon was outgassed for at least 48 hr in a vacuum of the order of  $10^{-6}$  mm Hg at 950 °C. Frumkin and co-workers found an exponential relationship between the oxygen pressure and the acid adsorption, and like Shilov found very little increase in adsorption when the pressure was increased above 20 mm Hg. These results were confirmed by Bretschneider (1932). Lepin (1931) found a similar behaviour for the adsorption of fatty acids provided they contained less than five carbon atoms. With higher homologues physical adsorption became of predominant importance.

Shilov and Chmutov (1930) proposed two basic oxides on the surface of the carbon; one to account for the adsorption of acid that was dependent on the oxygen pressure, the other to account for the residual adsorption on what they believed to be a completely outgassed carbon. This was opposed by Frumkin because if the adsorption of an acid by an H-carbon was a neutralization process, the adsorption should occur within a narrow pH interval of 2-3 units. His experimental results showed that adsorption occurred over a much wider span of pH values. Frumkin's objections to Shilov's theory have been summarized by Kuchinsky, Burstein, and Frumkin (1940).

Frumkin's school proposed an alternative "electrochemical theory" according to which the adsorption of electrolytes on the carbon would be determined by the electrical potential at the carbon-solution interface, and by the capacity of the double layer. The magnitude of the potential would be determined by the presence of electrochemically active gases on the surface of the carbon. If oxygen was introduced to the carbon suspension at room temperature the carbon, according to this theory, would lose electrons, become positively charged, and attract anions from the solution. A platinized carbon would behave similarly, but acquire a slightly higher potential. A non-platinized carbon in the presence of hydrogen gas at room temperature would not attract cations but would do so if platinized. Such a platinized H-carbon would become negatively charged when suspended in aqueous solutions and acquire a diffuse double layer of hydrogen ions which could be exchanged for the cations of an added salt. Frumkin believed that at least some of the adsorption of alkali by L-carbons is due to the presence of chemisorbed hydrogen which would be electrochemically active and behave as a hydrogen electrode even although unplatinized H-carbons would not adsorb alkali in the presence of molecular hydrogen at room temperature (Burstein 1937).<sup>\*</sup> No explanation could be given for the charging process. In their later papers Frumkin and his co-workers restricted the electrochemical theory to the adsorption of acids having a normality

<sup>\*</sup> Frumkin's concept that carbon containing chemisorbed hydrogen behaves as a hydrogen electrode has been criticized by Kolthoff (1927) and Kruyt and de Kadt (1931). This criticism has led to the rejection of his theory as a whole by later workers, but it does not appear to have been realized that that part of his theory concerning the adsorption of acids by non-platinized carbons in the presence of oxygen is based on considerable experimental evidence that has been confirmed by others, and is fully justified.



less than 0.02 since physical adsorption was considered to be appreciable in more concentrated solutions.

Steenberg (1944) objected to the basic oxide theory of Shilov "since substances of a corresponding nature and stability are not known in organic chemistry", and since it failed to account for the many observations that inorganic salts of organic bases are adsorbed on H-carbons with a decrease in the pH of the solution.\* According to Steenberg the organic part of an organic-inorganic electrolyte was physically adsorbed on the surface of the carbon (primary adsorption), whereas the accompanying oppositely charged inorganic ions formed a diffuse double layer, as in an ion-exchange adsorbent, and were said to be secondarily adsorbed. Hydrolytic adsorption could be satisfactorily accounted for by considering the Donnan equilibrium between the secondarily adsorbed ions and the ions in the free solution. According to his theory adsorption of inorganic acids involved primary adsorption of protons, by physical forces, and secondary adsorption of the anions. The anion of an adsorbed acid could be displaced by a different anion of a salt added to the carbon, the relative affinities being those of the Hofmeister series. Exchange constants were calculated for a variety of systems. An adsorbed inorganic acid could be displaced from the carbon by shaking it with an aqueous suspension of a water-immiscible solvent in which the acid was insoluble. This was taken as evidence for physical adsorption of the acid and the "basic oxide theory" was discounted. Steenberg's results show, however, that in no instance was it possible to completely desorb the acid from the carbon even although a volume of water-immiscible solvent was used which was greater than that of the solution from which the acid was originally adsorbed. This suggests that at least some of the acid may not be adsorbed physically. The experimental fact that acid adsorption from dilute solutions requires molecular oxygen was not accounted for by Steenberg's theory.

## II. PHYSICAL OR CHEMICAL ADSORPTION OF ACID?

The adsorption isotherms of hydrochloric acid on a series of carbon blacks that have been heated in nitrogen to 800 °C are given in Figure 1 and those on two sugar carbons activated in air for different times at 800 °C are given in Figure 2. In a parallel series of experiments, toluene was added to study desorption effects as described by Steenberg. These results are also given in Figures 1 and 2.

Whereas the adsorption of acid on the carbon prepared from the ink black, "Black Pearls 2", is considerably influenced by toluene, that adsorbed on the carbon prepared from the furnace black "Kosmos 20" is not affected at all at acid concentrations below 0.4N. The behaviour of the carbon prepared from the channel black "Spheron 3" is intermediate between these two extremes. The results with the sugar carbons show that the influence of toluene increases with activation time. We have not been able to prepare a carbon which can adsorb 375 mg/g of methylene blue chloride in 5 min as obtained by Steenberg.

\* Adsorption processes on carbon that are accompanied by a change in pH have been termed "hydrolytic adsorption".

Nor could we prepare a carbon such that 86 per cent. of the adsorbed acid could be displaced by toluene. This difference in behaviour might be attributed to the influence of different catalytic ash constituents in the carbons which could be expected to influence the rate of combustion of carbon during activation and thus affect the porosity and surface area of the product.

Whereas differences in porosity could account for the different influence of toluene on the desorption of acid from sugar carbons, no such influence could account for the inability of toluene to affect the adsorption of acid on "Kosmos 20" since furnace blacks are essentially non-porous. The results can be accounted for if part of the adsorption is physical and can therefore be affected

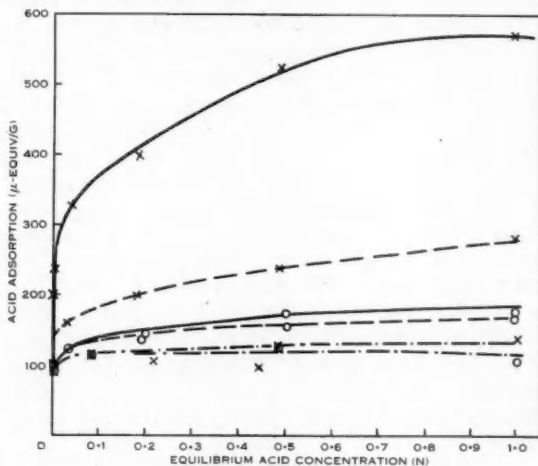


Fig. 1.—The influence of toluene on the adsorption isotherms of hydrochloric acid on various carbon blacks after heating in nitrogen at 800 °C.

— "Black Pearls 2"; — "Spheron 3";  
 - - - "Kosmos 20"; × without toluene; ○ with toluene.

by toluene, and if the remainder is due to a chemical factor which cannot be influenced by toluene. If the sites at which acid is chemically adsorbed are susceptible to oxidation and tend to be destroyed during the activation process, the influence of toluene should increase with activation time as is experimentally observed with the sugar carbons. Similarly, the greater influence of toluene on the carbon prepared from "Black Pearls 2" as compared with "Kosmos 20" could be attributed to the influence of oxidation during the manufacture of the ink black.

Bruns and Psychov (1931) showed that when a dry carbon was exposed to dry ozone it lost its ability to adsorb acid at low concentrations but acquired the ability to adsorb alkali. At higher concentrations, acid was adsorbed and the shape of the adsorption isotherm suggested physical adsorption. This

behaviour suggests that some of the acid may be chemically adsorbed at sites which were destroyed by ozone and which acquired the properties of an acid on oxidation.

As described above it has been conclusively established that an H-carbon that has been thoroughly outgassed does not adsorb acid from dilute solutions in the absence of molecular oxygen. When oxygen was admitted acid was adsorbed in amounts equivalent to the oxygen adsorbed provided the acid concentration was very low (Frumkin, Burstein, and Lewin 1931). According to Frumkin oxygen absorption was only appreciable in the presence of acid. This effect suggests a chemical reaction between the carbon and the oxygen that is responsible for the removal of acid from such solutions.

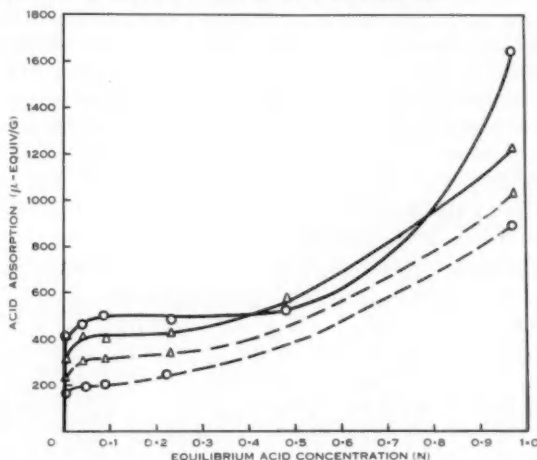
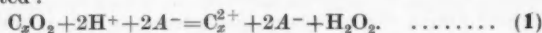


Fig. 2.—The influence of toluene on the adsorption isotherms of sugar carbons activated in air at 800°C.

△ 13 hr activation; ○ methylene blue adsorption 3 mg/g;  
 ○ 48 hr activation, methylene blue adsorption 113 mg/g;  
 — without toluene; — — with toluene.

Bretschneider (1932) compared the adsorption of hydrochloric acid on aerated and outgassed carbons. The isotherms were parallel, except at very low concentrations of the acid. This suggested to Bretschneider that part of the adsorbed acid was chemically adsorbed by oxides on the surface, and this part was independent of acid concentration. The remainder was considered to be physically adsorbed.

It has been shown by Lamb and Elder (1931), Kolthoff (1932), and King (1933) that a peroxide-like substance may be extracted with acid from a carbon that has been exposed to moist air. More recently, Burstein and Frumkin (1941) showed that the adsorption of acid by carbon in the presence of oxygen was accompanied by the liberation of hydrogen peroxide. The following reaction was suggested:



Their results showed that considerably less than the amount of peroxide predicted by equation (1) was liberated but this was attributed to the known ability of the carbon to catalyse the decomposition of hydrogen peroxide.

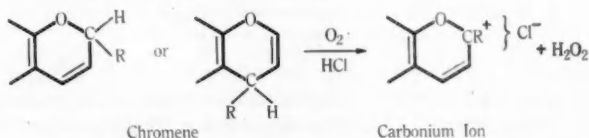
Winslow (1947) showed that an H-carbon acquired a strong oxidizing potential when oxygen was bubbled through a suspension of the carbon in acid. After exposure to oxygen, the suspension was able to oxidize considerable amounts of ferrous iron. These results also support the observations that a peroxide-like substance is liberated from the carbon.

It may be concluded from the above experiments, that the adsorption of mineral acids on an H-carbon from very dilute solutions is predominantly a chemical phenomenon, associated with the oxidation of the carbon by molecular oxygen resulting in the production of hydrogen peroxide and a basic structure in the carbon, whereas for more concentrated solutions physical adsorption occurs in addition. The basicity of sugar carbon and carbon blacks cannot be due to basic nitrogen, since the latter is essentially absent from these carbons. Nor is it likely to be related to a carbon structure alone, since carbons heated to temperatures of about 800 °C show a marked decrease in basicity yet their carbon content steadily increases as oxygen is removed. Shilov suggested that it is related to oxygenated structures. Pyrylium salts are familiar examples of groups containing basic oxygen.

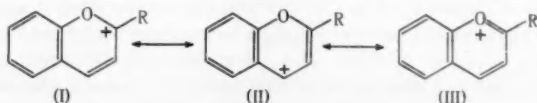
### III. CHROMENE AND CARBONIUM ION STRUCTURES IN H-CARBONS

The foregoing observations may be satisfactorily explained by the presence in H-carbons of pyran structures. The pyran structures are of course conjugated with the aromatic layer planes of the carbon, and for simplicity will in future be referred to as chromene (benzpyran) structures. The chemistry of simple chromenes has been reviewed by Wawzonek (1951). The chromene structure is a heterocyclic oxygen-containing ring involving an activated  $>\text{CH}_2$  or  $>\text{CHR}$  group.

A characteristic reaction of this group is the formation of a carbonium ion according to the following equation :

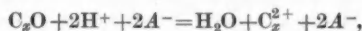


Well-known benzopyrylium derivatives are the anthocyanidins which may be represented as resonance hybrids involving the structures I, II, and III. Their



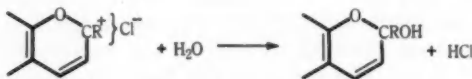
behaviour will be discussed in terms of the 2-carbonium structure I. The divalent oxidation of a chromene group to a carbonium ion involves the adsorp-

tion of one equivalent of acid per four equivalents of oxygen. If allowance is made for the regeneration of oxygen by the decomposition of the hydrogen peroxide formed, a ratio of 1 : 2 should be observed for the equivalents of acid adsorbed and oxygen consumed, as measured from changes in pressure. Frumkin, Burstein, and Lewin's (1931) data indicated a ratio of approximately 1 : 1 for very dilute solutions. At higher acid concentrations more acid than oxygen was adsorbed (Bruns and Piloyan 1931). However, the validity of these early results is open to question since in his later paper with Burstein (Burstein and Frumkin 1941) Frumkin replaces his former equation



by equation (1) in which one equivalent of acid is adsorbed per *two* equivalents of oxygen. Kuchinsky, Burstein, and Frumkin (1940) observed that 2 farads are required for the desorption of one equivalent of acid by the cathodic polarization of a carbon electrode that had been equilibrated with acid and oxygen. This observation can be accounted for by the reduction of the carbonium ion form of the carbon to the chromene state. It is extremely difficult to accurately determine the stoichiometry of the adsorption of acid and oxygen by H-carbons since hydrogen peroxide is known to attack carbon and produce acid groups, and since it is also difficult to quantitatively distinguish between physically and chemically adsorbed acid. If future work can confirm Frumkin's early observations of a ratio of 1 : 1, it would suggest that the adsorption of acid by an H-carbon occurs not by the divalent oxidation of chromene groups but by the univalent oxidation of the "semiquinone" form of the chromene to carbonium ions. It may be shown that the electrochemical data, to be discussed in Section IV, are equally well accounted for by both alternatives. For convenience, the theory will be presented in terms of chromene structures.

The benzopyrylium ion is a weak base having a dissociation constant of the order of  $10^{-10}$  (Sondheimer 1953), and is partly hydrolysed by water to chromenol :



The experimental observation that it is extremely difficult to wash all the adsorbed acid from an H-carbon even if large quantities of water are used (Miller 1932) may be accounted for by the partial hydrolysis of carbonium ion salts in the carbon.\* The chromene structures postulated contain C—O—C and C=C linkages to the existence of which attention has previously been directed.

\* This behaviour makes it unlikely that the acid adsorbed from very dilute solutions is present as a true oxonium salt since the latter would be very readily hydrolysed. Oxonium salts are possibly formed at higher acid concentrations and may be the cause of the steep upward rise observed in this region of the adsorption isotherms (Fig. 2).

Villars (1948) has shown that the greater part of the oxygen in carbon blacks was unreactive towards the Grignard reagent and he has depicted it as ether oxygen.

Ether oxygen can be expected to arise in sugar carbons from condensation of hydroxyl groups during the process of charring. The presence of olefinic double bonds in sugar carbons and carbon blacks has been discussed previously (Garten and Weiss 1955). Recent studies of the production of carbon black in flames have suggested that the carbon arises from the polymerization of dienes produced by pyrolysis of the fuel (Thorp, Long, and Garner 1955; Ruven Smith and Gorden 1956). This mechanism could account for the presence of olefinic double bonds in carbon blacks. Such bonds could arise in sugar carbons by dehydration.

In Part I of this series (Garten, Weiss, and Willis 1957), it was shown that n- and f-lactones can be produced by air oxidation at 400 °C of an H-carbon prepared at 800 °C. The alkali adsorption of the series of sugar carbons, "Carbolac 1", and commercial carbon blacks studied in Part I is given in Table 1. The adsorption of hydrochloric acid in the presence of toluene is also reported for these carbons. The influence of toluene on the adsorption of acid has been discussed in Section II. Toluene should not influence the adsorption of acid by the chromene groups but may be expected to desorb physically adsorbed acid on sites accessible to toluene and acid. The adsorption of acid in the presence of toluene may therefore provide a semiquantitative measure of chromene concentration. The uncertainty lies in the possible influence of porosity on the quantitative aspects of the test. The results show that in the "Carbolac 1" and sugar carbon series there is a converse relationship between chromene concentration and alkali adsorption, and that the carbons prepared at 800 °C contain the maximum concentration of chromene structures. In the series of commercial carbon blacks, it is seen that the chromene concentration per unit of surface area is a maximum for the furnace black and is much lower for the channel and ink blacks. These results suggest that lactone groups have been produced, at least in part, by the oxidation of chromenes. Such an oxidation could give rise to n- $\delta$ -lactones. This is reasonable in view of the known fact that chromenes (containing  $>CH_2$ ) are oxidized to lactones (Baker 1929) and provide some chemical evidence for the concept of chromene groups in H-carbons. It is not suggested, however, that all lactone groups present in L-carbons arise from oxidation of chromene structures. Winslow (1947) showed that a carbon that has not been exposed to acid and oxygen will rapidly reduce permanganate. This reducing capacity is roughly proportional to the oxidizing capacity of the carbon towards ferrous iron in acid solution in the presence of oxygen. Once the carbon has been exposed to acid and oxygen, it no longer reacts rapidly with permanganate. Winslow considered these results indicated that a peracidic rather than a peroxidic complex was present on the surface of a carbon exposed to acid and oxygen since peracids, unlike peroxides, will not react with permanganate. An alternative explanation is that permanganate oxidizes the chromene groups of an H-carbon. If these have already been oxidized (by oxygen) they can no longer react with permanganate. This

interpretation is supported by the fact that, as referred to above, cold dilute permanganate solutions are known to oxidize simple chromenes to coumarins (Baker loc. cit.). It is therefore possible that the amount of permanganate consumed in the fast reaction is a measure of the number of accessible chromene

TABLE I

THE CHROMENE CONCENTRATION IN VARIOUS CARBONS AS MEASURED BY THE ADSORPTION OF ACID IN THE PRESENCE OF TOLUENE

Carbon	Alkali Adsorption* ( $\mu$ -equiv/g)	Chromenes ( $\mu$ -equiv/g)	Chromenes ( $\mu$ -equiv/ 100 m <sup>2</sup> )†
"Carbolac 1", original	1800	4	
Heated to			
400 °C .. .. .	1740	8	
500 °C .. .. .	1540	8	
600 °C .. .. .	1060	15	
700 °C .. .. .	610	57	
800 °C .. .. .	230	104	
"Carbolac 1" heated to 800 °C and then to			
400 °C .. .. .	590	40	
500 °C .. .. .	520	85	
600 °C .. .. .	400	95	
700 °C .. .. .	290	117	
Sugar char heated to			
400 °C .. .. .	590	45	
500 °C .. .. .	220	99	
600 °C .. .. .	140	279	
700 °C .. .. .	140	345	
800 °C .. .. .	130	315	
Sugar char heated to 800 °C and then to			
400 °C .. .. .	320	183	
500 °C .. .. .	270	235	
600 °C .. .. .	220	274	
700 °C .. .. .	180	303	
"Carbolac 1" .. .. .	1800	4	0.4
"Mogul A" .. .. .	1180	9	3
"Elf 0" .. .. .	580	11	7
"Spheron 3" .. .. .	400	37	—
"Spheron 6" .. .. .	370	10	8
"Spheron 9" .. .. .	460	11	11
"Kosmos 20" .. .. .	0	110	550

\* Based on results from Part I of this series (Garten, Weiss, and Willis 1957).

† Surface areas based on B.E.T. measurements reported in Part I (loc. cit.).

groups in a carbon, although the possibility must not be overlooked that other groups may be simultaneously oxidized.

The following sections will show how the new concept of chromene structures can interpret the known electrochemical and catalytic properties of H-carbons.

## IV. THE ELECTROCHEMISTRY OF H-CARBONS

If chromene structures occur on the surface of an H-carbon they will function as a redox system. In the presence of molecular oxygen and acid the carbon will be oxidized so that it acquires the potential of the oxygen-hydrogen peroxide couple with which it is in equilibrium. Hence, the adsorption of acid anions at the carbonium ion sites will be a function of the oxygen partial pressure and the pH value of the solution. It has been shown by Kutchinsky, Burstein, and Frumkin (loc. cit.) that if a carbon electrode is first equilibrated with acid and oxygen, acid that has been adsorbed in the process may be desorbed by applying a cathodic potential to the electrode in the presence of an inert atmosphere. They also showed that an H-carbon electrode, free from platinum, adsorbs alkali when it is cathodically polarized. Evidence has previously been presented from these laboratories that the latter behaviour is due to the reduction of quinone groups (Garten and Weiss 1955). Thus in acid solutions an H-carbon behaves as an anion-exchange adsorbent when oxidized, whereas in alkaline solutions the same carbon behaves as a cation-exchange adsorbent when reduced.

In the following, the behaviour of such redox systems in the carbon will be theoretically assessed and will be shown to be in reasonable quantitative agreement with the experimental facts. However, the complexity of the constants in the equations to be derived does not enable one, by fitting the equations to the experimental data, to obtain values for the dissociation constants and standard redox potentials of the electrochemically active groups of the carbon.

(a) *Adsorption as a Function of Potential*

As in the derivation of the equation for the redox potential of methylene blue it is necessary to consider the chromene as a very weak acid. The chromene-carbonium ion system may then be considered to be of the type



Since the ions must be considered as the potential producing species and if the system is reversible and concentrations are used in place of activities for a first approximation, the potential  $E_h$  will be given by the equation

$$E_h = E' - \frac{RT}{2F} \ln \frac{[\text{Red}^-]}{[\text{Ox}^+]}, \quad \dots \quad (2)$$

in which  $E'$  is a constant. For a given carbon sample the sum of the concentration of the oxidized species  $S_o$  and the reduced species  $S_R$  will be a constant

$$[S_R] + [S_o] = C,$$

where  $[S_R] = [\text{Red}^-] + [\text{Red}-\text{H}]$  and  $[S_o] = [\text{Ox}^+] + [\text{Ox}-\text{OH}]$ . If the dissociation constant of the chromene, considered as an acid, is  $K_R$ , then it can be shown that

$$[\text{Red}^-] = \frac{[S_R] \cdot K_R}{(K_R + [\text{H}^+])}, \quad \dots \quad (3)$$



and that

$$[S_R] = C - \frac{[Ox^+]( [H^+]K_0 + K_w )}{[H^+]K_0}, \quad \dots \quad (4)$$

where  $K_0$  is the dissociation constant of the carbonium salt, and  $K_w$  that of water.

Substituting for  $S_R$  in equation (3) and dividing by  $[Ox^+]$  it follows that:

$$\frac{[Red^-]}{[Ox^+]} = \frac{K_R \cdot C}{(K_R + [H^+])[Ox^+]} - \frac{K_R([H^+]K_0 + K_w)}{(K_R + [H^+])[H^+]K_0}$$

Let  $\alpha$  be the fraction of oxidized chromene which is present as carbonium ion. Then

$$[Ox^+] = \alpha \cdot C,$$

and  $\alpha$  will be proportional to the acid adsorbed by the oxidized carbon. Therefore,

$$E_h = E' - \frac{RT}{2F} \ln \left\{ \frac{K_R}{K_R + [H^+]} \right\} \cdot \frac{1}{\alpha} - \frac{K_R([H^+]K_0 + K_w)}{(K_R + [H^+])[H^+]K_0} \quad \dots \quad (5)$$

For a chromene in an acid solution  $[H^+] \cdot K_0 \gg K_w$  and  $H^+ \gg K_R$ , so that

$$E_h = \left\{ E' - \frac{RT}{2F} \ln \frac{K_R}{[H^+]} \right\} - \frac{RT}{2F} \ln \frac{1 - \alpha}{\alpha} \quad \dots \quad (6)$$

Kuchinsky, Burstein, and Frumkin (1940) have equilibrated an H-carbon electrode with acid and oxygen and then polarized it cathodically. As the positive potential of the carbon was reduced the adsorption of acid fell in the manner shown by the experimental points in Figure 3. Except in the region of maximum adsorption, where the acid adsorbed was appreciable in relation to that in the solution, the experiment was conducted at an approximately constant pH value of 2. Under these conditions it is possible to calculate the form of the relation between acid adsorption and potential according to the above equation. The calculated values are shown as the full line in Figure 3 and agree reasonably well with the experimental results within the limits of experimental error.

#### (b) Adsorption as a Function of Oxygen Pressure

The potential of the chromene-carbonium ion system on the H-carbon will be determined by that of the oxygen-hydrogen peroxide couple with which it is in equilibrium. In acid solutions, the concentration of the ionized species of hydrogen peroxide will be negligible compared with the undissociated form. Hence

$$[H_2O_2] = S_0.$$

If  $k_1$  and  $k_2$  are the dissociation constants of hydrogen peroxide, and if  $[H^+] \cdot K_0 \gg K_w$

$$[O_2^{2-}] = k_2 \cdot k_1 \cdot \frac{[Ox^+]}{[H^+]^2}.$$

The potential  $E$  of the oxygen electrode is given by

$$E = E^0 + \frac{RT}{2F} \ln \frac{p}{[O_2^2]},$$

where  $p$  is the partial pressure of the oxygen.

Equating  $E$  to  $E_h$  in equation (6)

$$E' - E^0 = \frac{RT}{2F} \ln \frac{p[H^+]K_R}{C \cdot k_2 \cdot k_1 \left( \frac{1-\alpha}{\alpha^2} \right)}.$$

For a constant pH value

$$p = Z \left( \frac{\alpha^2}{1-\alpha} \right), \quad \dots \dots \dots (7)$$

where  $Z$  is a constant.

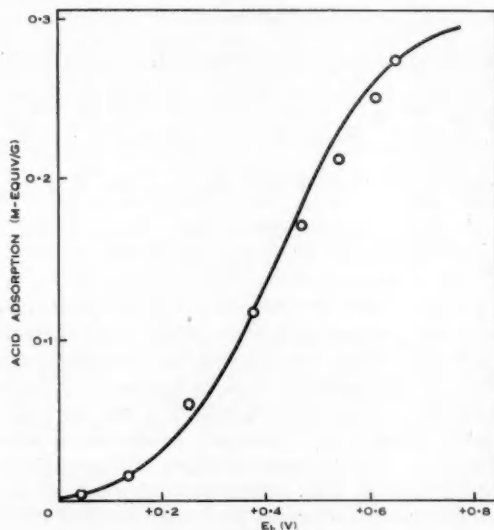


Fig. 3.—The cathodic polarization of an H-carbon electrode in a 0.01N solution of hydrochloric acid.  
 ○ Experimental points due to Kuchinsky, Burstein, and Frumkin (1940). The full line gives the theoretical curve.

This function is shown as the curve in Figure 4 and agrees well with the experimental points shown on it. The experimental data are from the paper by Frumkin, Burstein, and Lewin (1931). The increased acid adsorption in the presence of ozone may be attributed to its greater redox potential.

#### (c) Potential as a Function of pH

Since a proton is involved in the chromene-carbonium ion transformation of H-carbon its potential will be a linear function of pH. This has been shown to be so experimentally by Kutchinsky, Burstein, and Frumkin (loc. cit.) and by Mizuno (1949).

## (d) Adsorption as a Function of pH

Kuchinsky, Burstein, and Frumkin (loc. cit.) pointed out that if the adsorption of acid is due to the neutralization of a weakly basic surface oxide, the adsorption should change from a maximum to zero over a pH range of a few units, which applies also to the above carbonium ion theory. This behaviour is not in accordance with their observations that the acid adsorbed from a salt solution at different pH values falls off rapidly in the pH range 0-4 and then much more slowly at higher pH values. The adsorption in the latter pH region is very small. A possible interpretation is that acid is adsorbed as a consequence

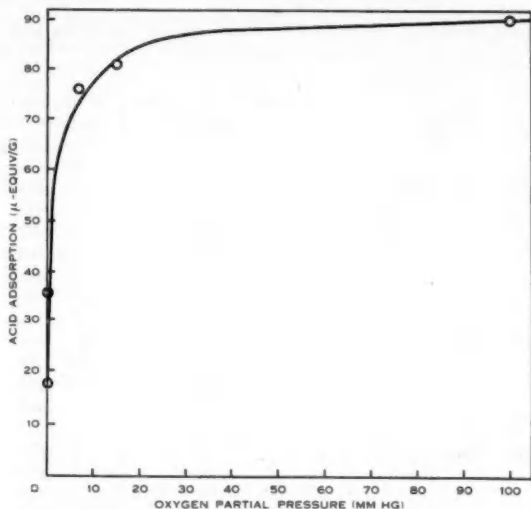


Fig. 4.—The influence of the partial pressure of oxygen on the adsorption of hydrochloric acid on an H-carbon.

○ Experimental points due to Frumkin, Burstein, and Lewin (1931). The full line gives the theoretical curve.

of the oxidation of chromenes, this being the major process in the region of low pH values, and also to some extent by physical adsorption, as claimed by Steenberg. Physical adsorption would account for the small uptake of hydrogen ions observed at the higher pH values.

## (e) The Adsorption of Alkali by H-Carbons

Garten and Weiss (loc. cit.) showed that an H-carbon, which normally will not adsorb alkali, does so if it is electrochemically reduced. This was taken as evidence for the presence of quinone groups in H-carbons, since the hydroquinone produced by reduction of a quinone would consume alkali.

Studebaker *et al.* (1956) have since concluded that 1,4-quinones are present in commercial carbon blacks since they consumed hydrogen on treatment with sodium borohydride, and since nitrogen was introduced on methylation with

diazomethane. The latter was considered to add to the 2,3-double bond of a 1,4-quinone to form a pyrazoline ring. The known thermal instability of these groups was considered to account for the fact that the quinone content, calculated from the nitrogen so introduced, was considerably lower than that deduced from the borohydride measurements. According to their interpretation of these results the quinone concentration was the greatest for the ink blacks. Table 2 shows the alkali adsorption of the ink black "Carbolac 1" heated in nitrogen to 800 °C, "Carbolac 1" itself, and sugar carbons activated at 400 and 800 °C after reduction with sodium borohydride, according to the method of Studebaker

TABLE 2  
THE ALKALI ADSORPTION OF VARIOUS CARBONS BEFORE AND AFTER REDUCTION  
WITH SODIUM BOROHYDRIDE

Carbon	Alkali Adsorption Blank ( $\mu$ -equiv/g)	Alkali Adsorption Reduced Carbon ( $\mu$ -equiv/g)
"Carbolac 1" .. .. .	1618	1574
	1618	1578
	1618	1592
	1630	1598
	1596	1598
	1600	1590
"Carbolac 1" heated to 800 °C ..	360	332
	368	328
	356	340
	360	340
Sugar char heated to 400 °C ..	322	278
	320	280
	302	314
	302	316
Sugar char heated to 800 °C ..	72	68
	72	66
	80	76
	80	74

*et al.*, and after thorough washing with acid and water. Blank experiments were performed in which the addition of the sodium borohydride was omitted. A number of repetitions were made to assess the experimental error. The results show no significant increase in acidity after reduction, from which it follows that if quinone groups are reduced they are reduced to a stage beyond that of the hydroquinone, or that quinone groups in the carbon are not reduced under these conditions or that quinone groups are absent. Thus the claim of Studebaker *et al.* that the ink black "Carbolac 1" contains the maximum amount of quinone groups of all the carbon blacks studied remains to be proven, and the use of sodium borohydride, under these conditions at least, as a method for the quantitative estimation of quinone groups in carbons cannot be justified. It

is therefore concluded, that either quinone groups are reduced beyond the hydroquinone stage or that a group other than quinone must be responsible for the oxidation of the borohydride. The formation of pyrazoline rings can be accounted for by the reaction of diazomethane with quinonoid double-bonds created by the opening of  $\beta$ -lactone rings during methylation.

The reduction of quinone groups in H-carbons by molecular hydrogen, if the carbon is platinized, provides a simple explanation for the adsorption of alkali by these carbons, as observed by Frumkin, Burstein, and Lewin (*loc. cit.*), if it is postulated that the platinum can catalyze such a reduction. The reduction of quinones to hydroquinones can also account for the observations of Kuchinsky, Burstein, and Frumkin that a non-platinized H-carbon electrode adsorbs alkali cations when cathodically polarized.

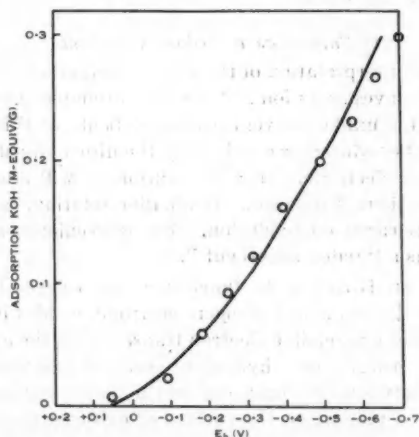
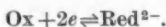


Fig. 5.—The cathodic polarization of an H-carbon in a solution of 0.0108N potassium hydroxide.  $\circ$  Experimental points due to Kuchinsky, Burstein, and Frumkin (1940). The full line gives the theoretical curve.

The quinone-hydroquinone system is of the following type



Using analogous arguments to those in Section IV (a) it may be shown that

$$E_h = E'' - \frac{RT}{2F} \ln \frac{\alpha}{C_1 - C_2 \alpha},$$

where  $C_1$  and  $C_2$  are constants and  $\alpha$  is the fraction of original quinone groups reduced and ionized.

The results of Kuchinsky, Burstein, and Frumkin (*loc. cit.*) plotted in Figure 5 show that some slight adsorption of alkali occurs at zero-potential. This may be attributed to adsorption at sites other than hydroquinone; for

example at lactone or phenolic groups. Such adsorption  $k$  will be independent of potential. If  $A$  is the total adsorption of alkali:

$$A = \alpha[C] + k$$

where  $[C]$  is the total quinone concentration in the original carbon. Substituting for  $\alpha$  in the above equation gives

$$E_h = E'' - \frac{RT}{2F} \ln \frac{A - k}{C_3 - C_4 A},$$

where  $C_3$  and  $C_4$  are algebraic functions of the hydrogen ion concentration and the two dissociation constants of the hydroquinone. The full line in Figure 5 is calculated from this equation and agrees reasonably well with Kuchinsky's data for a constant pH value.

#### (f) Carbon as a Redox Adsorbent

From the above interpretation of the experimental data it may be concluded that an H-carbon behaves as an ion and electron-exchange adsorbent. Activated carbon is a conductor unlike conventional adsorbents of this type. Hence its redox systems may be reduced or oxidized by the direct transfer of electrons if it is fabricated into an electrode. In acid solution, it will adsorb acid anions if oxidized and release them if reduced. In alkaline solution, cations are adsorbed on reduction and released on oxidation. For convenience such an adsorbent will be referred to as a "redox adsorbent".

The ability of an H-carbon to function as an oxygen-hydrogen peroxide electrode, and if platinized, as a hydrogen electrode, resides in the ability of its redox systems to effect a reversible electron transfer with the external gas couple. Platinum black also behaves as a hydrogen electrode and this may also be due to an equilibrium between hydrogen gas and a redox system of platonic acids that are known to be present on the surface of oxidized platinum (Pennycuik 1930).

### V. CATALYTIC PROPERTIES OF H-CARBONS

H-Carbons are effective catalysts for the oxidation of a variety of reductants by molecular oxygen. The literature of this subject will be reviewed elsewhere (Garten and Weiss 1957).

One such catalytic reaction is the oxidation of ferrous iron in acid solutions in the presence of an H-carbon. It will be shown that chromenes in the carbon can satisfactorily account for the kinetic results of Posner (1953).

In acid solution, some of the ferrous ion will be present as the anion  $\text{FeCl}_3^-$  which may be adsorbed at a carbonium ion site as shown in Figure 6.\* It is assumed that (i) there exists an equilibrium between the  $\text{FeCl}_3^-$  anion salt of the carbonium structure V, and its half-reduced state VI, which is a semiquinone; and that (ii) the latter, in the presence of atmospheric oxygen, forms a reversible

\* Whereas the anion  $\text{FeCl}_4^-$  is known to exist and is fairly stable in acid medium, little is known about  $\text{FeCl}_3^-$ . There seems, however, no intrinsic reason to exclude the existence of this complex, although it probably will be much less stable.

peroxide with the unpaired electron of the semiquinone, which is resonance stabilized to a high degree, VII. Whereas it is known (Lowenbein 1924) that ferric chloride will oxidize chromenes to benzopyrylium salts and that a semiquinone of a chromene is oxidized by oxygen in acid solutions, there is no literature evidence available to support assumption (i). However, the assumption leads to a kinetic scheme that conforms with the experimental results obtained by Posner, that is,

$$\frac{d[\text{Fe}^{3+}]}{dt} = \frac{K[\text{H}^+][\text{Fe}^{2+}][\text{O}_2][\text{C}]}{\Sigma \text{Fe}},$$

where  $[\text{C}]$  is the catalyst concentration and  $\Sigma \text{Fe} = [\text{Fe}^{2+}] + [\text{Fe}^{3+}]$ . The redox cycle in which the carbonium salt will oxidize  $\text{Fe}^{2+}$  and the intermediate free

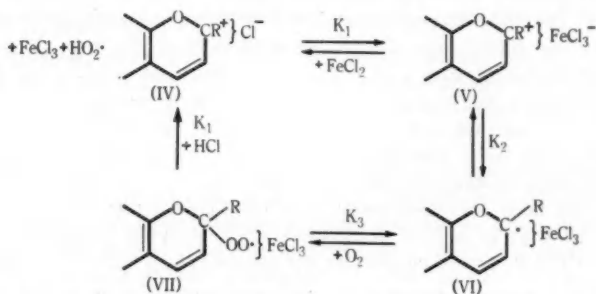
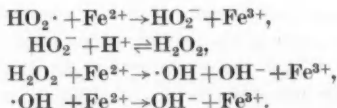


Fig. 6.—The catalytic oxidation of ferrous iron in the presence of oxygen and the chromene groups of an H-carbon.

radical be regenerated by air-oxidation is shown in Figure 6, where  $K_1$ ,  $K_2$ , and  $K_3$  are equilibrium constants,  $[P]$  is the concentration of structure V, and  $k_1$  is a rate constant. Thus

$$\frac{d[\text{Fe}^{3+}]}{dt} = \frac{d[\text{HO}_2\cdot]}{dt} = k_1 \cdot K_1 \cdot K_2 \cdot K_3 [\text{H}^+][\text{O}_2][\text{Fe}^{2+}][P],$$

the rate of  $\text{Fe}^{3+}$  production being actually four times as high because of the following Haber-Weiss scheme involving oxidation of  $\text{Fe}^{2+}$  by  $\text{HO}_2\cdot$ ,  $\text{H}_2\text{O}_2$ , and  $\cdot\text{OH}$ .



For convenience the reactions shown in Figure 6 are depicted occurring at one carbonium ion site but in an actual carbon such sites are interconnected by a system of conducting bonds. The single electron of the semiquinone is not necessarily located at the one site. Thus oxygen and ferric chloride may be simultaneously adsorbed at different sites on the carbon. A mechanism will

be proposed elsewhere for the oxidation of oxalic acid by oxygen in the presence of an H-carbon (Garten and Weiss 1957).

It is known that iron-carbon, and particularly iron-nitrogen-carbon complexes, enormously enhance the catalytic efficiency of an H-carbon. The subject will be reviewed elsewhere (Garten and Weiss 1957). This behaviour is probably that of a promoter in which the iron atom might facilitate the ability of the carbon to stabilize an unpaired electron. It might also facilitate the attachment of oxygen to the carbon.

#### VI. THE SIGNIFICANCE OF THE CHROMENE CONCEPT TO FUEL AND RUBBER TECHNOLOGY

Frey (1955) has observed that the overall reaction rate of carbon with oxygen over the temperature range 300–550 °C was decreased approximately 10-fold, and the initial rate of adsorption of oxygen was reduced more than 100-fold, by treatment with acid. This effect was attributed to the formation of a carbon-halogen bond by a reaction of the acid with surface oxides. In view of the evidence presented in this paper, it is probable that during the treatment of the carbon with acid chromene systems are oxidized to benzopyrylium (carbonium) ions leading to salt formation. As the initial rate of oxygen adsorption has been decreased more than 100-fold by treatment with acid, it would appear that in normal combustion in this range of temperatures the  $>\text{CH}_2$  or  $>\text{CHR}$  groups of chromenes are the sites most active towards oxygen.

The data in Figure 2 suggest that prolonged activation of a sugar carbon at 800 °C results in a gradual loss of these active sites. It is therefore possible that the development of internal surface area, which occurs during the process of activation, is due to selective combustion involving elimination of chromene structures.

As is well known in rubber technology, a characteristic property of furnace carbon blacks is their marked ability to produce "scorching" of an unvulcanized rubber-carbon mixture. This phenomenon may be regarded as a vulcanization at room temperature and is not observed with the channel blacks. From the data of Table 1, it is seen that the furnace black, "Kosmos 20", has a very high concentration of chromene groups, as compared with the channel blacks. The vulcanization of rubber and the drying of a drying oil is generally accepted to be due to the presence of methylene groups adjacent to olefinic double bonds in these compounds. During the process of vulcanization of rubber,  $\alpha$ -methylene groups are dehydrogenated by sulphur, resulting in a cross-linking of the rubber molecules either directly or via sulphur bridges. It is possible that the chromene  $>\text{CH}_2$  or  $>\text{CHR}$  groups of carbon undergo a similar reaction with rubber. These  $>\text{CH}_2$  or  $>\text{CHR}$  groups might be expected to be even more reactive than those in rubber. This reaction could account for scorching and would contribute to a cross-linking between carbon and rubber during vulcanization. Cross-linking could also result from polymerization with quinonoid double bonds as suggested in an earlier paper by Garten and Weiss (1955). Quinonoid double bonds could arise in channel blacks from the opening



of  $\gamma$ -lactone rings under alkaline conditions, and this might be one role of alkali during vulcanization.

Further research might profitably be directed to the development of more quantitative methods for the estimation of chromene groups and the relation of the latter to the known technical behaviour of different carbons.

#### VII. EXPERIMENTAL METHODS

(i) *Activation Procedure*.—The activated carbons were made according to the method of Steenberg (loc. cit.) and King (1937) from charred cane sucrose. One char was activated for 13 hr in 17 ml/min of moist air followed by treatment in a stream of dry air for 1 hr. It was then cooled in a stream of oxygen-free nitrogen. A second carbon was prepared from the same char by an identical procedure except that the activation time was increased to 48 hr.

(ii) *Methylene Blue Adsorption*.—Carbon (0.4 g) was shaken with 50 ml of 0.3 per cent. solution of methylene blue for 48 hr, filtered, and the methylene blue content of the filtrate determined by titration with titanous sulphate solution.

(iii) *Adsorption Isotherms*.—Samples of carbon (0.5 g) were each shaken with 25 ml of hydrochloric acid, of a strength between 0.01 and 1N for 48 hr, filtered and the acid concentration of the supernatant liquid determined by titration with standard alkali using bromothymol blue as the indicator. In a separate identical series 25 ml of toluene was added to each sample after 48 hr shaking with acid and the shaking was continued for a further 96 hr. The mixture was then filtered through a sintered glass filter, the phases were separated, and the aqueous layer titrated as before.

"Spheron 3" (after being heated in nitrogen to 800 °C) and "Kosmos 20" were treated in an identical manner except that 2.5 g samples of carbon were added to the 25 ml of acid to compensate for the reduced adsorption capacity of these carbons. Samples of "Black Pearls 2" (1 g), previously heated in nitrogen to 800 °C, were treated in an identical manner.

In a further series of experiments carbon (1 g) was shaken with 25 ml of 0.030N hydrochloric acid and then treated with 15 ml of toluene as above. The final acid concentration in the aqueous phase was determined. The acid adsorption so measured is given in Table 1 under chromene.

(iv) *Borohydride Reduction*.—To 3.00 g of carbon was added 20 ml of a 0.1N sodium hydroxide solution, containing 2.6 mmoles of sodium borohydride, and 40 ml of 0.1M boric acid. After standing for 2 hr, with occasional shaking, 7.5 ml of 2N sulphuric acid was added. The mixture was allowed to stand overnight and then filtered. The carbon was then boiled for 2 days with 1 l. of distilled water, decanted, and the procedure repeated three times. The carbon was then filtered and dried *in vacuo*. The alkali adsorption was determined as described in Part I of this series (Garten, Weiss, and Willis 1957). A blank experiment was performed in which the addition of sodium borohydride was omitted.

## VIII. ACKNOWLEDGMENTS

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## ARYLATION OF AROMATIC COMPOUNDS\*

### IV. IODOSOBENZENE DIBENZOATES WITH NITROBENZENE AND CHLOROBENZENE

By B. M. LYNCH† and K. H. PAUSACKER‡

[Manuscript received February 21, 1957]

#### Summary

When nitrobenzene reacts with iodosobenzene dibenzoate both nitrodiphenyls and nitrophenyl benzoates are formed. Isomer ratios are reported and discussed.

The reactions of iodosobenzene dibenzoate, di-*p*-toluate and dianisate with chlorobenzene have been investigated. The relative yields of the various products have been determined.

#### I. INTRODUCTION

Since this work was completed, Hey, Stirling, and Williams (1956) have investigated the reaction of iodosobenzene dibenzoate§ with nitrobenzene and have shown that it can effect phenylation. They have drawn analogies between the reactions of this reagent and benzoyl peroxide. The present work substantiates these findings but also shows that benzoyloxylation occurs simultaneously.

#### II. EXPERIMENTAL

##### (a) Reagents

Chlorobenzene and nitrobenzene were purified as already described in Part III of this series (Lynch and Pausacker 1957b). Iodosobenzene dibenzoate, m.p. 161 °C, was prepared by the action of iodosobenzene diacetate with a large excess of benzoic acid in diethyl ether (Fox and Pausacker 1957). Iodosobenzene di-*p*-toluate, m.p. 174 °C (Found: equiv. wt., 230, 234. Calc. for  $C_{22}H_{18}O_4I$ : equiv. wt., 237) and iodosobenzene dianisate, m.p. 189 °C (Found: equiv. wt., 248, 259. Calc. for  $C_{22}H_{18}O_6I$ : equiv. wt., 253) were prepared similarly in yields of 80 and 81 per cent. respectively.

##### (b) General Procedure

Reactions were carried out, and the various products separated and identified, following the method outlined previously in Parts I and III of this series (Lynch and Pausacker 1957a, 1957b).

\* For Parts I, II, and III of this series see Lynch and Pausacker (1957a, 1957b) and Pausacker (1957).

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§ It may be noted that this compound (Hey, Stirling, and Williams 1956; Fox and Pausacker 1957) has previously been termed phenyl iodosobenzoate. The alternative nomenclature is now regarded as preferable for compounds of this type.

## (c) Results

The results obtained are summarized in Tables 1 and 2. The values in parentheses are average yields in mol per mol of benzoyl peroxide.

TABLE 1  
REACTIONS OF NITROBENZENE WITH IODOSOBENZENE DIBENZOATE

Experiment No.:	2	4	6	7
PhI(OCOPh) <sub>2</sub> (g) .. ..	20	40	10	20
Ph·NO <sub>2</sub> (ml) .. ..	250	300	250	250
Temperature (°C) .. ..	139	139	154	160
Time of heating (hr) .. ..	16.5	9.75	7.5	4.3
Vol. CO <sub>2</sub> (ml) .. ..	550	995	230	445
	(0.54)	(0.50)	(0.44)	(0.44)
Ph·CO <sub>2</sub> H				
1st acid (g) .. ..	7.30	13.3	3.87	6.87
	(1.34)	(1.22)	(1.24)	(1.28)
2nd acid (g) .. ..	0.71	1.66	0.52	1.08
	(0.13)	(0.15)	(0.20)	(0.19)
Nitrodiphenyls (g) .. ..	3.50	7.01	1.42	2.90
	(0.40)	(0.39)	(0.32)	(0.33)
Phenols (g) .. ..	0.56	1.67	0.50	1.02
	(0.09)	(0.13)	(0.16)	(0.16)
High-boiling residue (g) ..	—	1.49	0.46	1.31

TABLE 2  
REACTIONS OF CHLOROBENZENE WITH IODOSOBENZENE DIBENZOATE, IODOSOBENZENE DI-*p*-TOLUATE,  
AND IODOSOBENZENE DIANISATE

Experiment No.:	2, 3	16, 17	19, 20
Substituent .. ..	—	<i>p</i> -Me	<i>p</i> -OMe
Wt. (g) .. ..	12.1, 12.8	13.6, 13.6	14.5, 14.5
Vol. PhCl (ml) .. ..	160, 160	160, 160	160, 160
Temperature (°C) .. ..	130	130	130
Time of heating (hr) .. ..	13.5, 13.8	12.8, 13.5	12.0, 12.2
Vol. CO <sub>2</sub> (ml) .. ..	513, 609	446, 492	487, 474
	(0.85)	(0.73)	(0.76)
ArCO <sub>2</sub> H ..			
1st acid (g) .. ..	2.8, 2.8	3.7, 3.1	3.9, 3.9
	(0.84)	(0.88)	(0.89)
2nd acid (g) .. ..	1.1, 1.3	1.2, 1.1	0.7, 0.7
	(0.34)	(0.30)	(0.16)
Phenol (g) .. ..	0.2, 0.3	0.05, 0.15	0.15, 0.10
	(0.06)	(0.04)	(0.04)
Diphenyls (g) .. ..	2.9, 2.9	3.0, 3.25	4.5, 4.2
	(0.56)	(0.52)	(0.69)
B.p. diphenyls .. ..	103–109 °C/0.15 mm 124–127 °C/1.2 mm	114–126 °C/0.15 mm	127–145 °C/0.1 mm
High-boiling residue (g)	0.4, 0.4	0.4, 0.6	1.1, 1.6

## (d) Ratios of Isomers Formed by Phenylation and Benzoyloxylation of Nitrobenzene

(i) *Phenylation*.—The mixture of nitrodiphenyls was analysed by a standard ultraviolet spectrophotometric method. A Hilger Uvispek spectrophotometer was used, and calibration spectra of the three isomeric nitrodiphenyls in absolute ethanol were recorded in the wavelength range 2100–3200 Å. The concentrations ( $10^{-5}$  mole/l) of the solutions were: 2-nitrodiphenyl, 2.01; 3-nitrodiphenyl, 2.05; and 4-nitrodiphenyl, 2.17. The spectra of two homogenized mixtures (from experiment No. 2) in ethanol were recorded, the concentrations being  $3.13 \times 10^{-5}$  mole/l. The extinction coefficients of the two mixtures were virtually identical, so the mean was used for the calculations. The mean percentage composition was found to be 2-nitrodiphenyl, 58; 3-nitrodiphenyl, 9; 4-nitrodiphenyl, 33; the overall error being  $\pm 4$  per cent.

(ii) *Benzoyloxylation*.—As a trial experiment showed that 2-, 3-, and 4-nitrophenols could be separated from an artificial mixture by chromatography on alumina (cf. Zechmeister 1950), the nitrophenol fraction from experiment 2 (0.56 g) was dissolved in benzene and chromatographed on acid-washed alumina. Three bands were obtained: bright orange, yellow-orange, and yellow-green. Elution of the bright orange band with benzene and benzene: ethanol (1:1) afforded 2-nitrophenol (0.28 g), m.p. and mixed m.p. 44 °C. The yellow-orange band was eluted with benzene: ethanol (1:5), yielding 3-nitrophenol (0.07 g), m.p. and mixed m.p. 95 °C. The yellow-green band was extruded and extracted (Soxhlet) with ethanolic 5N hydrochloric acid yielding a yellow amorphous solid (0.11 g), m.p. 105–130 °C, which was converted into 2,6-dibromo-4-nitrophenol, m.p. and mixed m.p. 142 °C, by bromination in acetic acid. Thus, of the nitrophenols separated, 61 per cent. consists of the 2-isomer, 15 per cent. of the 3-isomer, and 24 per cent. of the 4-isomer. However, recovery of 4-nitrophenol is probably not quantitative.

TABLE 3  
MEAN ISOMER RATIOS OF PHENYLATION AND BENZOYLOXYLATION OF  
NITROBENZENE

	2-Isomer %	3-Isomer %	4-Isomer %
Phenylation (Hey, Stirling, and Williams 1956) ..	57.5	14	28.5
Phenylation (Present work)	58	9	33
Benzoyloxylation (Present work) .. .. .	61(—)	15(—)	24(+)

## III. DISCUSSION

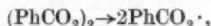
The results with nitrobenzene are in general agreement with those reported by Hey, Stirling, and Williams (1956) and a similar isomer ratio of the nitrodiphenyls is observed. In addition, it is seen that the isomer ratio of the nitrophenol mixture is closely similar (Table 3). Thus, like naphthalene (Lynch and Pausacker 1957*b*), the same isomer ratio occurs in both phenylation

and benzyloxylation. The average molar ratio of benzyloxylation products to phenylated products in nitrobenzene experiments 2, 4, 6, and 7 is 0.37, thus showing that benzyloxylation is an important simultaneous reaction. This ratio is higher than that observed (0.14) when benzoyl peroxide reacts with nitrobenzene at 78 °C (Lynch and Pausacker 1957*b*).

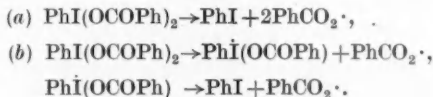
The yield of "1st acid" is very high and a balanced equation could only be written for this reaction if it were assumed that partial hydrolysis of the iodosobenzene dibenzoate takes place. This has already been suggested by Hey, Stirling, and Williams (1956). Due to the uncertainty of the amount of hydrolysis, balanced equations are not written for these systems.

The results with chlorobenzene show that less hydrolysis is occurring in these reactions but the "1st acid" is still significantly higher than the diphenyls formed. It should be noted that the ratio of benzyloxylation to phenylation in the reaction of chlorobenzene with iodosobenzene dibenzoate is 0.11, indicating a much lower reactivity towards radical attack than nitrobenzene (cf. Lynch and Pausacker 1957*b*).

It has been found that the temperature required for the reaction of iodosobenzene dibenzoate with chlorobenzene and nitrobenzene is approximately 50 °C higher than that required for an equal rate of reaction of benzoyl peroxide with these solvents. In addition, 0.11*M* iodosobenzene dibenzoate in benzene lost only 5 per cent. of its oxidizing power after refluxing for 100 hr, whereas the corresponding reaction with benzoyl peroxide is quite rapid. This difference in reactivity is probably explained by the fact that only one oxygen-oxygen bond is broken in the dissociation of benzoyl peroxide into benzyloxy radicals, that is,



whereas two iodine-oxygen bonds must be broken in the dissociation of iodosobenzene dibenzoate into iodobenzene and benzyloxy radicals. This may involve either simultaneous (*a*) or successive (*b*) processes:



It is seen from Table 2 that the introduction of *p*-methyl and *p*-methoxyl substituents into iodosobenzene dibenzoate does not significantly alter the yields of the various products formed. This is in agreement with a previous observation (Pausacker 1957) that introduction of these substituents has little effect on the relative amounts of the reaction products formed from benzene and substituted benzoyl peroxides.

One notable difference between the reactions of chlorobenzene with benzoyl peroxide and iodosobenzene dibenzoate is that the amount of high-boiling residue is reduced significantly when iodosobenzene dibenzoate is used. The ratio of the weights of high-boiling residue to chlorodiphenyls is *c.* 1.0 when benzoyl

peroxide reacts with chlorobenzene (Lynch and Pausacker 1957b) and yet only c. 0.14 when iodosobenzene diacetate is used. Similar results are noted with *p*-dichlorobenzene (Karelsky and Pausacker, unpublished data).

#### IV. ACKNOWLEDGMENT

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## METHYLSTEROIDS\*

### III. REDUCTION OF KETONES DERIVED FROM LANOSTEROL

By C. S. BARNES† and A. PALMER‡

[Manuscript received March 20, 1957]

#### Summary

The base catalysed hydrogen transfer from solvent alcohol to carbonyl groups is studied with 7,11-dioxolanostan-3 $\beta$ -yl acetate (I; R=Ac) and shown to give almost entirely 3 $\beta$ ,7 $\beta$ ,11 $\beta$ -trihydroxylanostane (V; R=R'=H) and the epimeric 3 $\beta$ ,7-dihydroxylanostan-11-ones (VI and VIII; R=H). Generalizations are made to account for their formation and stereochemistry.

The four 3 $\beta$ ,7,11-trihydroxylanostanes are prepared.

#### I. INTRODUCTION

The Wolff-Kishner method with various modifications has been used extensively in the steroid field for the elimination of carbonyl groups. In the past few years the 7-oxo-group has been selectively removed from 7,11-dioxo-compounds which were intermediates in synthesis of adrenal cortical hormones (Chamberlain *et al.* 1951; Heusser *et al.* 1951; Fieser *et al.* 1951, 1953; Tsuda and Hayatsu 1955). In most cases the yield of the desired 7-deoxy-compound was low or not stated. Selective reduction of the 7-oxo-group of I (McGhie, Pradhan, and Cavalla 1952) has produced 11-oxolanostanol in 47 per cent. yield.

Barton, Ives, and Thomas (1955) have applied a modified Wolff-Kishner reduction to the dione (I) and obtained lanostanyl acetate in 69 per cent. yield. Using a similar method we found the yield to decrease as the quantity of hydrazine was reduced, and the work described in the sequel resulted from an examination of this last reaction.

#### II. WOLFF-KISHNER REDUCTION OF DIOXOLANOSTANOL

7,11-Dioxolanostanyl acetate (I; R=Ac) was reduced with hydrazine in diethylene glycol in the presence of the corresponding sodium alkoxide, using a weight of hydrazine somewhat less than that of the diketone. Chromatography on alumina of the acetylated product gave three compounds besides lanostanyl acetate (II; R=Ac) which was isolated in 10 per cent. yield.‡

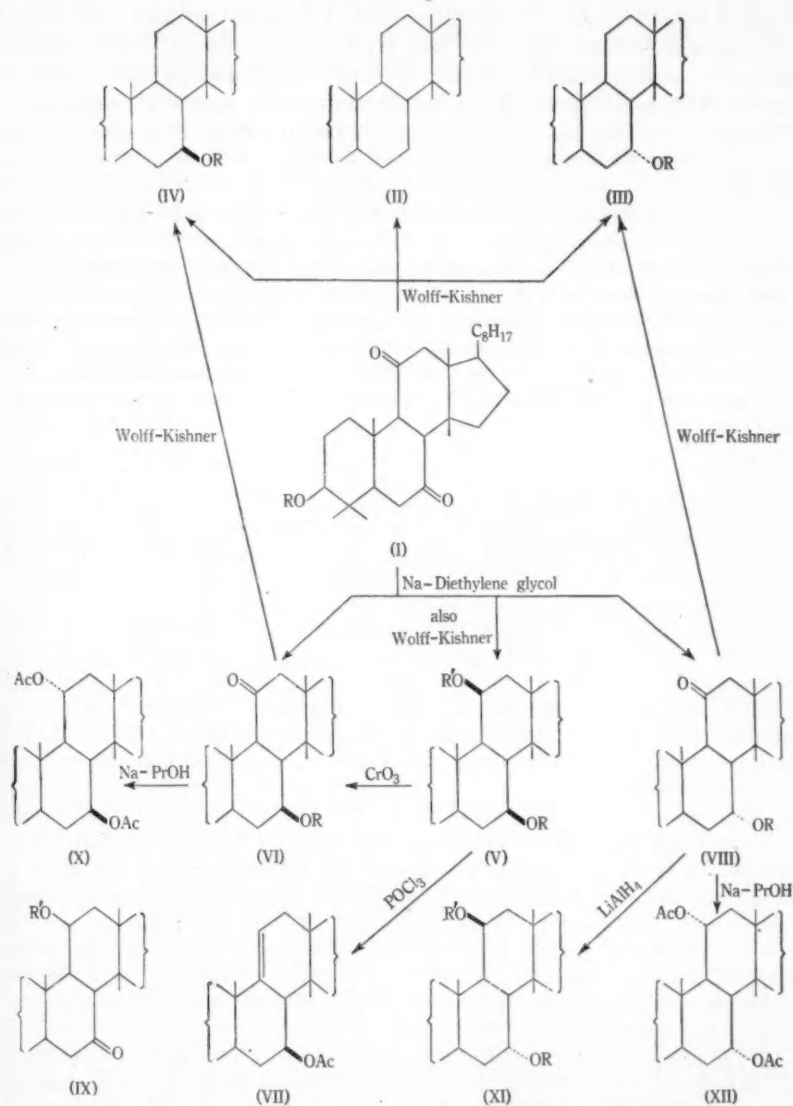
The two more easily eluted compounds (yields 10 and 20%) analysed as isomeric diacetates and had constants in agreement with those obtained by

\* Part II of this series see Barnes (1956).

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‡ All yields quoted are approximate and are minimum values because of the difficulty in completely resolving the complex mixtures of chemically similar compounds.





Barton and Thomas (1953) for the epimeric 3 $\beta$ ,7-diacetoxylanostanes (III; R=Ac, and IV; R=Ac). Both were characterized as the diols. The third compound (15 per cent. yield) was more strongly absorbed on alumina and had m.p. 235 °C,  $[\alpha] +56^\circ$ . Although these constants did not agree well with

those obtained by previous workers (m.p. 238 °C,  $[\alpha] +70^\circ$  by Voser *et al.* (1950); Cavalla and McGhie (1951)) it was shown to be the 3 $\beta$ ,7,11-trihydroxylanostane 3,7-diacetate (V; R=Ac, R'=H) of these authors since it gave a ketone (VI; R=Ac) on oxidation and an olefin (VII; R=Ac) on dehydration (Cavalla and McGhie 1951). Furthermore V (R=Ac, R'=H) was characterized by acetylation with acetic anhydride and perchloric acid to a triacetate (V; R=R'=Ac).

These last three reactions together with the resistance to base catalysed acetylation are characteristic of an 11 $\beta$ -hydroxyl group. Reduction of the derived ketone (VI; R=Ac) using anhydrous hydrazine with sodium in diethylene glycol, followed by acetylation of the product gave 3 $\beta$ ,7 $\beta$ -diacetoxylanostane (IV; R=Ac). Hence V (R=Ac, R'=H) has a 7 $\beta$ -acetoxyl group and is formulated as 3 $\beta$ ,7 $\beta$ ,11 $\beta$ -trihydroxylanostane 3,7-diacetate. The derived ketone (VI; R=Ac) is therefore 3 $\beta$ ,7 $\beta$ -diacetoxylanostan-11-one and the olefine (VII; R=Ac) obtained by dehydration is 3 $\beta$ ,7 $\beta$ -diacetoxylanost-9(11)-ene.

### III. BASE TREATMENT OF DIOXOLANOSTANOL

Reduction of carbonyl compounds to alcohols by primary alcohols in the presence of alkali is a well-known reaction (see references cited by Hargreaves and Owen (1947) and Elks and Philipps (1956)), and alcohols frequently occur as by-products from Wolff-Kishner reductions (Dutcher and Wintersteiner 1939; Wintersteiner and Moore 1946a, 1946b; Djerassi, Ringold, and Rosenkranz 1954; Striebel and Tamm 1954) although for less hindered carbonyls their occurrence may be reduced by using a large excess of hydrazine (Dutcher and Wintersteiner 1939) or by the method of Huang-Minlon (1949). It was of interest, therefore, to determine the effect of base and solvent alone on I. The diketone (I) was heated overnight in a solution of diethylene glycol with the corresponding sodium alkoxide at about 200 °C, and the acetylated product chromatographed.

The most easily eluted compound VIII (R=Ac) had m.p. 195–196 °C,  $[\alpha] +11^\circ$  and analysed as an oxodiacetate isomeric with VI (R=Ac). The next eluted pure compound was VI (R=Ac) (Cavalla and McGhie 1951) identical with that obtained previously. Yields isolated were 10 and 20 per cent. respectively. Although the separation of VI (R=Ac) and VIII (R=Ac) on the chromatogram was not complete, it is considered unlikely that the intermediate unresolved fractions contained a third substance for when some of these fractions were crystallized, by hand picking they could be separated into the two pure compounds.

The compound VIII (R=Ac) was shown to be a diacetate by hydrolysis to an oxodiol (VIII; R=H) which gave with benzoyl chloride in pyridine a dibenzoate (VIII; R=Bz) having  $\lambda_{\max}$  230 m $\mu$ ,  $\epsilon$  26,000. An 11 $\beta$ -hydroxyl group therefore was absent. The presence of a carbonyl group and possibly of an axial hydroxyl was shown by perchloric acid catalysed dehydration of the diol (VIII; R=H) to give a crude product having the ultraviolet absorption of a conjugated enone ( $\lambda_{\max}$  255 m $\mu$ ). It follows that the hydroxyl was probably

7 $\alpha$  with the oxo-group at the 11-position. Finally, VIII (R=Ac) gave 3 $\beta$ , 7 $\alpha$ -dihydroxylanostane (III; R=H) on modified Wolff-Kishner reduction and is therefore formulated as 3 $\beta$ , 7 $\alpha$ -diacetoxylanostan-11-one.

The most strongly absorbed fraction from the acetylated product was purified by further chromatography and crystallization to give mainly V (R=Ac, R'=H) (yield 15 per cent.). A higher melting (250 °C) portion was obtained in small yield (2 per cent.), but could not be satisfactorily purified. Analysis and its strong adsorption on alumina indicated that it may possibly be the 11 $\beta$ -epimer of IX (R=Ac, R'=H).

Increasing the reaction time to 3 days did not change the pattern of the products except that the high melting minor component was not detected. As isolated from this last experiment, V (R=Ac, R'=H) again had a rotation lower than that previously recorded by other workers but in agreement with that now obtained from the Wolff-Kishner reduction. The presence of an inseparable contaminant of low rotation was suspected and the isolated V (R=Ac, R'=H) was acetylated with acetic anhydride-perchloric acid and the triacetate V (R=R'=Ac) chromatographed. In this way a small quantity of a compound, analysing as the diacetate (IX; R=R'=Ac) was obtained, which had  $[\alpha] +64^\circ$ . This therefore was not decreasing the rotation of V (R=Ac, R'=H). Purified triacetate (V; R=R'=Ac) was converted to triol with lithium aluminium hydride and reacylated with acetic anhydride in pyridine to V (R=Ac, R'=H) which again had constants in agreement with those above (m.p. 235 °C,  $[\alpha] +56^\circ$ ). The melting point in a sealed evacuated tube was raised to 245–246 °C. We conclude that these are the correct constants for 3 $\beta$ , 7 $\beta$ , 11 $\beta$ -trihydroxylanostane 3,7-diacetate (V; R=Ac, R'=H).

It is of interest to note that even after overnight treatment with sodium in hot diethylene glycol no unreacted I was obtained and that the total reaction product consisted mainly of V, VI, and VIII.

#### IV. THE EPIMERIC 3 $\beta$ ,7,11-TRIHIDROXYLANOSTANES

Besides V, three other 3 $\beta$ ,7,11-trihydroxylanostanes are possible. One of these, the triequatorial 3 $\beta$ , 7 $\beta$ , 11 $\alpha$ -triol, was obtained as the triacetate (X) by Barnes *et al.* (1953) by sodium in propanol reduction (and acetylation) of I (R=Ac). The triequatorial configuration was assumed from the method of formation which is known to favour formation of equatorial hydroxyl groups (Barton 1953).

Recently, Elks and Phillipps (1956) have drawn attention to the fact that a compound formed similarly from an ergosterol analogue of I and also assumed to have the triequatorial configuration, did in fact have a 7 $\alpha$ -axial hydroxyl group. Therefore, it was advisable to check the configuration of the triacetate of Barnes *et al.* (1953a) by a synthesis unambiguous with regard to the 7-position. Reduction of VI (R=Ac) which has a 7 $\beta$ -acetoxyl group, by sodium-propanol gave a product which after acetylation by acetic anhydride-pyridine was easily eluted from alumina by benzene. The 11-oxo-group had therefore been reduced to the expected 11 $\alpha$ -hydroxyl. Constants of the resulting triacetate

were in agreement with those reported and the melting point was not depressed on mixing with a sample prepared as previously (Barnes *et al.* 1953). We conclude that the assigned  $3\beta$ ,  $7\beta$ ,  $11\alpha$ -triacetoxyl structure for X is correct.

Reduction of VIII ( $R=Ac$ ) by two reasonably stereospecific methods gave the remaining triols XI and XII. Firstly, VIII ( $R=Ac$ ) was reduced with lithium aluminium hydride and the acetylated (acetic anhydride-pyridine) product absorbed on alumina. The strongly absorbed hydroxylic main product gave the diacetate (XI;  $R=Ac$ ,  $R'=H$ ). This was characterized by further acetylation (acetic anhydride-perchloric acid) to give  $3\beta$ ,  $7\alpha$ ,  $11\beta$ -triacetoxylanostane (XI;  $R=R'=Ac$ ).

Reduction of VIII ( $R=Ac$ ) by sodium-propanol and acetylation (acetic anhydride-pyridine) gave the easily eluted  $3\beta$ ,  $7\alpha$ ,  $11\alpha$ -triacetoxylanostane (XII;  $R=Ac$ ) as main product.

#### V. DISCUSSION

While our work was in progress Elks and Phillipps (1956) reported the alkali catalysed hydrogenation of  $3\beta$ -acetoxyergost-22-ene-7,11-dione, an ergosterol analogue of I. At the temperature of refluxing ethanol with potassium hydroxide, products analogous to VI and VIII resulted, with the latter, having an axial-hydroxyl group predominating. On the basis of the postulated mechanism (see also Woodward, Wendler, and Brutschy 1945) the preponderance of the thermodynamically less stable axial hydroxyl group was rationalized. The formation of larger quantities of the epimer with the thermodynamically more stable equatorial hydroxyl from similar reactions at a higher temperature (Dutcher and Wintersteiner 1939) was attributed to equilibration (Windaus 1916).

It is now possible to make two further generalizations: First, that *the less hindered the carbonyl group the more easily it is reduced*. Thus in our work compounds VI and VIII resulted by initial reduction of the relatively less hindered 7-oxo group, while substances of type IX in which the relatively more hindered 11-oxo-group was reduced first were minor components. This conclusion follows because the hydrogen donating body can approach the less hindered position more easily. Second, that *the more hindered the carbonyl group the greater will be the predominance of axial hydroxyl formed*. Thus from the 7-oxo-group of I substantial quantities of each of the epimeric 7-hydroxy compounds (VI and VIII) resulted, while from the more hindered 11-oxo-group only the axial  $11\beta$ -hydroxy derivatives (V and IX) were obtained. Elks and Phillipps (1956) provide no data on the reduction of the 11-oxo-group. However, they account for only 50 per cent. of their starting material and it would appear that much of their product was left adsorbed on the chromatographic alumina. Since unchanged starting material would be easily eluted and detected with the 7-acetoxy-11-oxo compounds it would appear that the material left adsorbed was unacetylated and therefore mainly  $11\beta$ -hydroxy compounds.

If this is correct, Elks and Phillipps' reduction of the acetoxyergostendione supports the second generalization. It is impossible to deduce from their

recorded results the fate of the 7-oxo-group of the strongly adsorbed fraction, but presumably it was largely  $3\beta$ ,  $7\beta$ ,  $11\beta$ -trihydroxyergost-22-ene 3,7-diacetate.

Two factors may operate to increase the formation of axial hydroxyl groups at sterically hindered positions. First, as the position becomes more hindered the hydrogen donor is forced to approach more from the less hindered equatorial direction, to give an equatorial hydrogen and hence an axial oxygen. Then, once formed, the axial hydroxyl may retain its configuration because equilibration is reduced at the more hindered position.

The fact that a greater amount of equatorial hydroxyl is produced at the 7-position of I when compared with the amount of equatorial hydroxyl from its ergosterol analogue cannot be admitted as evidence relating to the operation of the first factor so long as the yields from the ergosterol analogue can be viewed with suspicion, because of losses through adsorption during chromatography.

Regarding equilibration of the hydroxyl groups it is apparent that no epimerization occurred with the highly hindered  $11\beta$ -compound since no  $11\alpha$ -hydroxy compound was detected even though the  $11\alpha$ -group would be thermodynamically favoured. At the less hindered 7-position the proportion of thermodynamically more stable  $7\beta$ -hydroxy compound formed was greater with the high temperature reduction in diethylene glycol on I than with the low temperature reduction in ethanol on the dioxoergostene by Elks and Philipps. If the ratio of products given by these workers is correct it would suggest that equilibration had occurred at the higher temperature. However that this was not likely is seen from reactions of the epimeric 7-hydroxy-11-oxo compounds (VI and VIII).

When  $3\beta$ ,  $7\beta$ -diacetoxylanostan-11-one (VI;  $R=Ac$ ) was reduced with anhydrous hydrazine in diethylene glycol with the rigorous exclusion of water it was converted in good yield to the 11-deoxy compound (IV;  $R=H$ ). With even traces of water, as when commercial ethanol (99 per cent.) was used as solvent at  $180^\circ C$ , the product was a mixture from which V ( $R=Ac$ ,  $R'=H$ ) was isolated in major yield by crystallization as the acetate.

In contrast, the  $7\alpha$ -hydroxy compound (VIII) under similar conditions where water was rigorously excluded gave the 11-deoxy compound (III) in small yield while the remainder was found to be mainly unreacted starting material. Again it was found that traces of water would suppress the carbonyl-eliminating reaction, but that in this case hydrogenation did not occur and the starting material was recovered. These experiments showed that the axial  $7\alpha$ -hydroxyl group is stable under the conditions used in the sodium diethylene glycol reduction and, therefore, V did not arise by way of VIII, but was formed directly from I. The relative stability of the 11-oxo-group of VIII to both Wolff-Kishner reduction and to hydrogenation is believed to be real and is attributed to the extra hindrance of the additional axial  $7\alpha$ -group. This explains the absence of the triol (XI) from the sodium-diethylene glycol reduction of I, which is surprising since it would otherwise be expected to arise from VIII in a like manner to V from VI.

## VI. EXPERIMENTAL

(a) *General*.—Melting points are corrected, and taken in open capillary tubes unless otherwise stated. Analyses are by Dr. K. W. Zimmermann, C.S.I.R.O. Microanalytical Laboratory at the University of Melbourne. All rotations were measured at  $20 \pm 2^\circ \text{C}$  in chloroform solution at a concentration of 1–2 per cent. using the sodium D-line. The absorption spectra were measured in ethanol solution. Light petroleum refers to the fraction b.p.  $60\text{--}80^\circ \text{C}$ .

(b) *Wolff-Kishner Reduction of 7,11-Dioxolanostan-3 $\beta$ -yl Acetate (I; R=Ac)*.—The method used with anhydrous hydrazine was similar to that of Barton, Ives, and Thomas (1955) except that hydrazine was distilled into a separatory funnel and a measured volume added to the reaction mixture.

Sodium metal (30 g) was dissolved in freshly distilled diethylene glycol (800 ml), and the diketone (I; 40 g) added. After heating to  $200^\circ \text{C}$  the anhydrous hydrazine (30 ml; c. 10M parts) was added. After 24 hr at  $180^\circ \text{C}$ , lower boiling fractions were removed by distillation to raise the temperature of the solution to  $220^\circ \text{C}$ , and the refluxing continued for 24 hr. The product was worked up in the usual way, acetylated (acetic anhydride-pyridine on the steam-bath), and then chromatographed on alumina (Peter Spence type H 500 g) to give 14 fractions (400 ml eluates).

The first fraction (11 g) eluted with light petroleum was rechromatographed (18 fractions). Light petroleum-benzene mixtures eluted lanostanyl acetate (II; R=Ac), which, after recrystallization had m.p.  $137\text{--}140^\circ \text{C}$ ,  $[\alpha] +46^\circ$ , and the correct analysis. Benzene eluted 3 $\beta$ ,7 $\alpha$ -diacetoxy lanostane (III; R=Ac; 3.2 g) which crystallized from chloroform, m.p.  $170\text{--}171^\circ \text{C}$ ,  $[\alpha] -20^\circ$  (Found: C, 77.1; H, 10.9; O, 11.8%. Calc. for  $\text{C}_{30}\text{H}_{48}\text{O}_4$ : C, 76.9; H, 11.0; O, 12.1%). Lithium aluminium hydride reduction gave 3 $\beta$ ,7 $\alpha$ -dihydroxy lanostane (III; R=H) which crystallized from methanol, m.p.  $156\text{--}158^\circ \text{C}$ ,  $[\alpha] +5^\circ$ . Further elution with benzene gave 3 $\beta$ ,7 $\beta$ -diacetoxy lanostane (IV; R=Ac; 1.4 g) which crystallized from chloroform-methanol, m.p.  $187\text{--}188.5^\circ \text{C}$ ,  $[\alpha] +40^\circ$  (Found: C, 77.2; H, 10.6%). Hydrolysis gave the diol (IV; R=H), m.p.  $207\text{--}9^\circ \text{C}$ ,  $[\alpha] +33^\circ$  (Found: C, 80.8; H, 12.0; O, 7.2%).

Fractions 3–7 (8 g) of the original chromatogram were eluted by benzene. They were combined and rechromatographed (alumina 500 g) to give 15 fractions (200 ml eluates), which followed a similar pattern to that preceding, except the 3 $\beta$ ,7 $\beta$ -diacetate, m.p.  $187\text{--}188^\circ \text{C}$ , predominated.

Fractions 10 and 11 (13 g) of the original chromatogram were combined and rechromatographed (15 fractions) to give mainly the 3 $\beta$ ,7 $\beta$ -compound on benzene elution, and 3 $\beta$ ,7 $\beta$ ,11 $\beta$ -trihydroxy lanostane 3,7-diacetate (V; R=Ac, R'=H) on elution with benzene-ether mixtures. After crystallizing several times from chloroform-methanol, m.p.  $234\text{--}236^\circ \text{C}$ ,  $[\alpha] +55^\circ$  (in a vacuum,  $244\text{--}245^\circ \text{C}$ ).

Total yields of the isolated compounds were:

	(g)	(%)
Lanostanyl acetate .. .. .	4.0	10
3 $\beta$ ,7 $\alpha$ -Diacetoxy lanostane .. .. .	3.5	9
3 $\beta$ ,7 $\beta$ -Diacetoxy lanostane .. .. .	8.0	20
3 $\beta$ ,7 $\beta$ ,11 $\beta$ -Trihydroxy lanostane 3,7-diacetate .. .. .	4.0	10
	—	—
	49	—

The 3 $\beta$ ,7 $\beta$ ,11 $\beta$ -trihydroxy lanostane 3,7-diacetate (V; R=Ac, R'=H) was characterized by chromic-acetic acid oxidation (Cavalla and McGhie 1951) to give 3 $\beta$ ,7 $\beta$ -diacetoxy lanostan-11-one (VI; R=Ac), m.p.  $170\text{--}171^\circ \text{C}$ ,  $[\alpha] +52^\circ$  (Found: C, 75.0; H, 10.2%. Calc. for  $\text{C}_{30}\text{H}_{46}\text{O}_5$ : C, 75.0; H, 10.4%). Dehydration with phosphorus oxychloride-pyridine (Cavalla and McGhie 1951) gave 3 $\beta$ ,7 $\beta$ -diacetoxy lanost-9(11)-ene (VII), m.p.  $212\text{--}214^\circ \text{C}$ ,  $[\alpha] +58^\circ$ . The same olefin was obtained when perchloric acid (1 drop) was added to a solution of the 11 $\beta$ -hydroxy compound (V; R=Ac, R'=H; 500 mg) in acetic anhydride (20 ml).

The 11 $\beta$ -hydroxyl group was acetylated by dissolving the 11 $\beta$ -hydroxy compound (100 mg) in acetic acid (40 ml), and 10 ml of a solution made by adding perchloric acid (72%; 1 drop) to acetic anhydride (100 ml) was added, after cooling the solutions in ice. After standing 6 hr at 0°C, and working up 3 $\beta$ ,7 $\beta$ ,11 $\beta$ -triacetoxylanostane (V; R=R'=Ac) crystallized from methanol, m.p. 191–192°C,  $[\alpha] +61^\circ$  (Found: C, 73.6; H, 10.1%. Calc. for C<sub>36</sub>H<sub>56</sub>O<sub>6</sub>: C, 73.4; H, 10.3%).

(c) *Base Treatment of 7,11-Dioxolanostan-3 $\beta$ -yl Acetate (I; R=Ac).*—(i) Sodium (10 g) was dissolved in diethylene glycol (500 ml), the dioxo-compound (I; R=Ac; 25 g) added and the temperature maintained at 180–190°C for 18 hr. Working up in the usual way gave a gummy product which from solution in light petroleum, slowly deposited crystals (2.4 g). These had m.p. 226–228°C and were chromatographed. Elution with benzene (9 fractions) gave V (R=Ac, R'=H; 2 g), m.p. 232–235°C after crystallization from methanol. Elution with ether gave two fractions (0.5 g), m.p. 250–257°C after crystallization from chloroform-methanol. All the mother liquors were evaporated and combined with the light petroleum solution from which the crystals were originally deposited, and then chromatographed on alumina (chromatogram A).

Elution with light petroleum gave five fractions (A<sub>1–5</sub>; 11.2 g); with light petroleum-benzene mixtures, three fractions (A<sub>6–8</sub>; 6.3 g); with benzene, six fractions (A<sub>9–14</sub>; 3 g); and with ether, four fractions (A<sub>15–18</sub>; 3.6 g).

Fraction A<sub>1</sub> (8.2 g) was rechromatographed to give five fractions (2.7 g) which were crystallized from methanol to give 3 $\beta$ ,7 $\alpha$ -diacetoxylanostan-11-one (VIII; R=Ac), m.p. 195–196°C,  $[\alpha] +11^\circ$  (Found: C, 75.2; H, 10.4%. Calc. for C<sub>34</sub>H<sub>54</sub>O<sub>5</sub>: C, 75.0; H, 10.4%). The following eight fractions (3.2 g) were obvious mixtures, and from the following five fractions (benzene; 2 g) there crystallized from chloroform-methanol 3 $\beta$ ,7 $\beta$ -diacetoxylanostan-11-one (VI; R=Ac), m.p. 176–177°C,  $[\alpha] +51^\circ$ , characterized by hydrolysis to the diol (VI; R=H) which, after crystallization from methanol, had m.p. 214–215°C,  $[\alpha] +55^\circ$ .

Fractions A<sub>9–17</sub> (5.2 g) on chromatography gave mainly 3 $\beta$ ,7 $\beta$ ,11 $\beta$ -trihydroxylanostane 3,7-diacetate (V; R=Ac, R'=H) which crystallized from methanol to have a m.p. somewhat variable with the rate of heating, but about 235–238°C. The same sample in a sealed evacuated tube had m.p. 244–245°C. Rotation of the several times recrystallized material was  $[\alpha] +60^\circ$ . The compound was further characterized by oxidation to the 11-ketone (VI; R=Ac), m.p. 175–176°C, undepressed on mixing with that obtained by the two methods above.

Fraction A<sub>18</sub> (1.4 g) deposited plates from methanol which after several crystallizations had m.p. 253–259°C,  $[\alpha] +40^\circ$  and was possibly mainly 3 $\beta$ ,11 $\beta$ -dihydroxylanostan-7-one 3-acetate (IX; R=Ac, R'=H) (Found: C, 77.2; H, 10.9%. Calc. for C<sub>32</sub>H<sub>54</sub>O<sub>4</sub>: C, 76.5; H, 10.8%).

(ii) In a similar experiment the dione (I; R=Ac; 30 g) was treated for 3 days at 180–190°C with sodium-diethylene glycol (20 g/700 ml). The acetylated product was chromatographed repeatedly as above to give (approx.) 3 $\beta$ ,7 $\alpha$ -diacetoxylanostan-11-one (VIII; R=Ac; 6 g), 20%; and 3 $\beta$ ,7 $\beta$ -diacetoxylanostan-11-one (VI; R=Ac; 3 g), 10%. The strongly absorbed fractions (7 g, 23%) were acetylated (acetic anhydride-perchloric acid at 0°C) and chromatographed. Light petroleum-benzene mixtures eluted fractions (600 mg), m.p. above 200°C. Benzene eluted 3 $\beta$ ,7 $\beta$ ,11 $\beta$ -triacetoxylanostane (5 g, 17%) crystallizing from methanol, m.p. 191–192°C,  $[\alpha] +64^\circ$ , m.p. undepressed on mixing with that obtained previously. The light petroleum-benzene fractions were recombined and again chromatographed to give probably 3 $\beta$ ,11 $\beta$ -diacetoxylanostan-7-one (300 mg), which after several recrystallizations from methanol had m.p. 220–221°C,  $[\alpha] +64^\circ$  (Found: C, 75.3; H, 10.5%. Calc. for C<sub>34</sub>H<sub>56</sub>O<sub>5</sub>: C, 75.0; H, 10.4%). The m.p. was depressed on admixture with V (R=Ac, R'=H), m.p. 235–238°C, or with VII (R=Ac), m.p. 210–212°C.

Hydrolysis of pure 3 $\beta$ ,7 $\beta$ ,11 $\beta$ -triacetoxylanostane (V; R=R'=Ac) was attempted by refluxing methanolic potassium hydroxide (5%; 1 hr). The product on acetylation with acetic anhydride-pyridine gave starting material V (R=R'=Ac), m.p. 191–192°C, undepressed on mixed m.p., instead of the 3,7-diacetate (V; R=Ac, R'=H). So reduction of the triacetox compound with lithium aluminium hydride in ether and similar acetylation was carried out,



giving 3 $\beta$ , 7 $\beta$ , 11 $\beta$ -trihydroxylanostane 3,7-diacetate, m.p. 235–236 °C (245–246 °C in a vacuum),  $[\alpha] +57^\circ$ .

(d) *Reactions of 3 $\beta$ , 7 $\alpha$ -Diacetoxyylanostan-11-one (VIII; R=Ac).*—(i) *Hydrolysis.* After hydrolysis of the diacetate (VIII; R=Ac) in refluxing methanolic potassium hydroxide and crystallization from light petroleum, 3 $\beta$ , 7 $\alpha$ -dihydroxylanostan-11-one (VIII; R=H) had m.p. 252.5–254.5 °C,  $[\alpha] +40^\circ$  (Found: C, 78.4; H, 11.5%. Calc. for C<sub>30</sub>H<sub>52</sub>O<sub>3</sub>: C, 78.2; H, 11.4%).

(ii) *Benzoylation.* Treating this diol (VIII; R=H) with benzoyl chloride in pyridine on the steam-bath gave the *dibenzoate* (VIII; R=Bz), which crystallized from chloroform-methanol, m.p. 255–257 °C,  $\lambda_{\text{max}}$  230 m $\mu$ ,  $\epsilon$  26,000 (Found: C, 79.0; H, 9.2%. Calc. for C<sub>44</sub>H<sub>62</sub>O<sub>5</sub>: C, 78.8; H, 9.3%).

(iii) *Dehydration.* The diol (VIII; R=H; 20 mg) was dissolved in acetic acid (3 ml) and perchloric acid (2 drops; 72%) added. After warming on a steam-bath (15 min) water was added. The precipitate was dried and was found to have  $\lambda_{\text{max}}$  255 m $\mu$ ,  $\epsilon$  1<sup>1</sup><sub>cm</sub> 190.

(iv) *Wolff-Kishner Reduction.* The carefully dried diacetate (VIII; R=Ac; 0.4 g) was heated 1.5 hr in solution of diethylene glycol and anhydrous hydrazine (2 ml). A solution of sodium-diethylene glycol (1 g/15 ml) was added and refluxing continued overnight. The acetylated product was chromatographed using light petroleum-benzene to give 3 $\beta$ , 7 $\alpha$ -diacetoxyylanostane (III; R=Ac; 50 mg), crystallizing from methanol, m.p. 170–171 °C (undepressed on mixing with that obtained previously),  $[\alpha] -20^\circ$ . Benzene eluted the starting material as shown by m.p. and mixed m.p. Only traces of the material were eluted with ether (absence of 11 $\beta$ -hydroxy compounds).

(v) *Lithium Aluminium Hydride Reduction.* The ketone (VIII; R=Ac; 100 mg) in anhydrous ether (50 ml) was reduced with the reagent (100 mg) at reflux temperature for 4 hr. After working up in the usual way and acetylating (acetic anhydride-pyridine) the product was applied on an alumina column and washed with benzene. Ether was then used to eluate 3 $\beta$ , 7 $\alpha$ , 11 $\beta$ -trihydroxylanostane 3,7-diacetate (XI; R=Ac, R'=H), crystallizing from acetone-methanol, m.p. 226–227 °C,  $[\alpha] +3^\circ$  (Found: C, 74.6; H, 10.7%. Calc. for C<sub>34</sub>H<sub>58</sub>O<sub>5</sub>: C, 74.7; H, 10.7%).

The diacetate (XI; R=Ac, R'=H; 20 mg) was acetylated with acetic anhydride-perchloric acid at 0 °C for 12 hr, and on crystallization from acetone-methanol gave 3 $\beta$ , 7 $\alpha$ , 11 $\beta$ -triacetoxyylanostane (XI; R=R'=Ac), m.p. 237–238 °C (245–246 °C in a vacuum),  $[\alpha] +17^\circ$  (Found: C, 74.1; H, 10.2%. Calc. for C<sub>38</sub>H<sub>60</sub>O<sub>6</sub>: C, 73.4; H, 10.4%).

(vi) *Sodium in Propanol Reduction.* The ketone (VIII; R=Ac; 150 mg) was dissolved in *n*-propanol (40 ml) and sodium metal added in small portions to the refluxing solution until it was saturated. After working up in the usual way the acetylated (acetic anhydride-pyridine) product was filtered through alumina in benzene solution. Crystallization from methanol gave 3 $\beta$ , 7 $\alpha$ , 11 $\alpha$ -triacetoxyylanostane (XII; R=Ac) (yield 80 mg), m.p. 157.5–158 °C,  $[\alpha] -18^\circ$  (Found: C, 73.4; H, 10.4%).

(e) *Reactions of 3 $\beta$ , 7 $\beta$ -Diacetoxyylanostan-11-one (VI; R=Ac).*—(i) *Base Catalysed Reductions.* The ketone (VI; R=Ac; 100 mg) in a sealed tube with sodium (100 mg) dissolved in 99% ethanol (10 ml) and anhydrous hydrazine (1 ml) was heated at 180 °C for 18 hr. Crystallization of the acetylated product gave the 3 $\beta$ , 7 $\beta$ , 11 $\beta$ -triol 3,7-diacetate (V; R=Ac, R'=H), m.p. 227–230 °C,  $[\alpha] +57^\circ$ .

(ii) *Wolff-Kishner Reduction.* The ketone (VI; R=Ac; 100 mg) was heated in diethylene glycol (5 ml) with anhydrous hydrazine (0.2 ml) for 2 hr, when a solution of sodium-diethylene glycol (100 mg/ml) was added. After heating (180 °C) for 18 hr the acetylated product crystallized from methanol, m.p. 184–185 °C,  $[\alpha] +41^\circ$ ; m.p. undepressed on mixing with 3 $\beta$ , 7 $\beta$ -diacetoxyylanostane.

(iii) *Sodium in Propanol Reduction.* The ketone (VI; R=Ac; 200 mg) was reduced as in Section VI (d) (vi). Crystallization from methanol gave 3 $\beta$ , 7 $\beta$ , 11 $\alpha$ -triacetoxyylanostane, m.p. 156–158 °C,  $[\alpha] +30^\circ$ ; m.p. undepressed on mixing with a sample prepared by the method of Barnes *et al.* (1953).



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## THE BINDING OF ZINC BY *S*-CARBOXYMETHYL KERATEINE 2 FROM WOOL

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### Summary

The binding of zinc from zinc acetate solution by the *S*-carboxymethyl derivative of kerateine 2 (SCMK2), a soluble protein extracted from reduced wool, has been studied by the method of equilibrium dialysis over the pH range 5.5 to 8.0 using radioactive  $^{65}\text{Zn}$  to determine the zinc concentration.

The binding increases as the pH increases from 5.5 to 7.5. The extent of binding is also a function of free zinc concentration, but it is not affected by changes in ionic strength between 0.15 and 1.0. The difference in solubility between the zinc complexes of the two protein components of SCMK2 is probably not due to the differences in the amount of zinc bound.

The binding of zinc is reversible over the concentration range studied at both pH 6.0 and 7.5, and its removal is accelerated by treatment with chelating agents.

Over the pH range 6.0 to 7.5 more zinc is bound by this protein than can be accounted for by histidine binding alone, assuming a 1:1 zinc-histidine ratio.

### I. INTRODUCTION

Kerateine 2, a soluble protein obtained from wool by fractional extraction with alkaline potassium thioglycollate (Gillespie and Lennox 1953, 1955*a*, 1955*b*), has recently been the subject of a number of chemical and physicochemical studies, both as the sulphydryl protein and as the *S*-carboxymethyl (SCMK2) derivative (Harrap 1955, 1956; Simmonds 1955; Gillespie 1956; Human 1956; O'Donnell and Woods 1956*a*, 1956*b*; Simmonds and Stell 1956).

Gillespie (1957) found that it was possible to fractionate the SCMK2 further by precipitation with zinc acetate. The larger part of the protein (P1) (about 90 per cent.) formed a water-insoluble zinc complex, which could easily be separated from the soluble (S1) portion of the protein. However, it was not known whether these fractions differed in their solubilities because of an unequal affinity for zinc or because of other factors. The SCMK2 and the P1-zinc complex were shown to be insoluble below about pH 4.5, while the P1-zinc complex was also very insoluble between pH 6 and 7. It was of interest to determine whether zinc binding was at a maximum or whether the low solubility in this region was due to the protein bearing a net charge close to zero. Another observation showed that between pH 6 and 7 the P1-zinc complex could be dissolved by raising the ionic strength to 0.5 or by repeatedly washing with distilled water, but it was not known whether this was due to the removal of bound zinc ions or to other effects. As the SCMK2 fractions were to be used for

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further physicochemical studies, some information was needed on the methods by which bound zinc could be completely removed from these proteins. The present study was undertaken to solve these problems.

The zinc binding of SCMK2 and its fractions was studied using the dialysis equilibrium technique of Klotz and co-workers (Klotz, Walker, and Pivan 1946; Klotz and Urquhart 1949; Hughes and Klotz 1956). The extent of binding was estimated by the use of radioactive zinc ( $^{65}\text{Zn}$ ) and was based on the work of Cohn *et al.* (1941) and Cunningham, Fischer, and Vestling (1955).

## II. MATERIALS AND METHODS

### (a) *Labelled Zinc Acetate*

Irradiated A.R. zinc dust (Atomic Energy Research Establishment, Harwell) with an initial radioactivity of 200  $\mu\text{C/g}$ , was dissolved in hydrochloric acid, precipitated as the carbonate, then dissolved in a slight excess of glacial acetic acid, and stored at  $+2^\circ\text{C}$  as a 0.05M zinc acetate solution.

### (b) *Preparation of the Wool Protein*

SCMK2 was prepared by the method of Gillespie and Lennox (1953), and Gillespie (1956), and stored at  $-20^\circ\text{C}$  until required. The S1 and P1 fractions were prepared as described by Gillespie (1957), but a second treatment with sodium citrate was undertaken and followed by dialysis.

### (c) *Equilibrium Dialysis*

The equilibrium dialysis technique of Klotz and his co-workers (Hughes and Klotz 1956) was used. The dialyses were carried out in 5 by 1 in. glass-stoppered Pyrex test tubes which were rocked at  $+2^\circ\text{C}$  for at least 72 hr. The system consisted of 15 ml protein solution (usually 0.5 per cent.) in Visking 22/32 "Cellophane" tubing, immersed in an external solution (25 ml) usually containing 10 ml of 2.0mM radioactive zinc acetate and varying amounts of non-radioactive zinc acetate to give final zinc concentrations ranging from 0.5 to 10mM. The dialysis tubing was boiled for 6 hr with several changes of glass distilled water before use. In studies on the effect of pH on binding, the buffer used in the system was a mixture of Tris (tris(hydroxymethyl)amino-methane) (0.085M), HCl (0.075M), and  $\text{CH}_3\text{COONa}$  (0.075M) giving a final ionic strength of 0.15, the pH being adjusted by the addition of acetic acid. In other experiments the buffers used were pH 7.5: Tris (0.085M), HCl (0.075M), KCl (0.075M); and at pH 6.0:  $\text{CH}_3\text{COONa}$  (0.075M),  $\text{CH}_3\text{COOH}$  (0.004M), KCl (0.075M).

### (d) *Measurement of Zinc Binding*

After dialysis the external solutions were decanted and the radioactivity measured. The radioactivity was also measured on a control 0.5mM  $^{65}\text{Zn}$  solution. The difference between the two counts divided by the count of the control 0.5mM zinc acetate solution gave the proportion of total zinc bound by the protein. Due allowance was of course made for a background of about 21 counts/min.

No corrections were made for the binding of zinc by "Cellophane" for, if this took place at all, it was well within experimental error. No detectable amount of protein dialysed through the membrane.

(e) *Measurement of Radioactivity*

Solutions were counted in a Geiger-Müller liquid counter tube (type MRC 2, capacity 19 ml) with a conventional scaling unit. When possible, counting was continued for a sufficient time to give a standard error of  $\pm 1$  per cent., but in background measurements and reversal of binding studies, the error was not greater than  $\pm 3$  per cent. No correction was necessary for decay, as the results were calculated from differences in the count observed on the same day between the control and test solutions.

(f) *Measurement of Protein Concentration*

Protein concentrations were measured using the micro-Kjeldahl procedure, assuming a nitrogen content for SCMK2 of 16.6 per cent., as determined for this protein by Mr. E. F. Woods in this Laboratory.

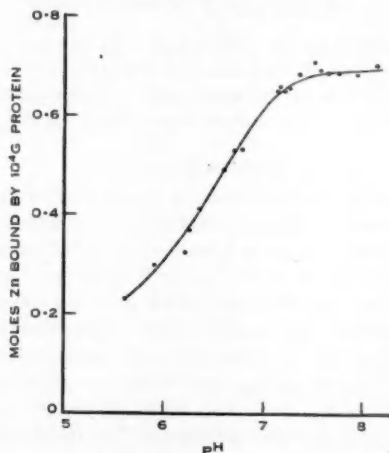


Fig. 1.—Effect of pH on the amount of zinc bound by SCMK2. Protein concentration 0.5 per cent., zinc concentration 0.5mM. Tris-acetate buffer, final  $I/2=0.15$ .

### III. RESULTS

(a) *The Relation between pH and Zinc Binding*

The effect of pH on the amount of zinc bound by SCMK2 was studied over the range of pH 5.5 to 8.0 at an initial zinc concentration of 0.5mM. The results are plotted in Figure 1. It can be seen that the amount of zinc bound increases with increase in pH from 5.5 to 7.5. There is no clear indication of any further increase above this pH, but the results are not decisive on this point.

*(b) The Relation between Concentration of Zinc Acetate and the Amount Bound*

This effect was studied using SCMK2 at pH 6.0 where the zinc protein complex is very insoluble, and at pH 7.5, where it is rather more soluble. The concentration of the  $^{65}\text{Zn}$  was 0.5mM, while the total zinc concentration ranged up to 10mM at an ionic strength of 0.15.

Figure 2 shows the relationship between free zinc concentration and the number of atoms of zinc bound by 10,000 g of protein. It can be seen that over the whole concentration range more zinc was bound at pH 7.5 than at pH 6.0, and that at the end of the concentration range studied the zinc binding had not reached a maximum.

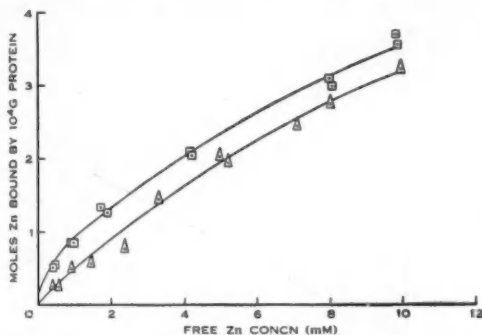


Fig. 2.—Effect of zinc concentration on the amount of zinc bound by 10,000 g of SCMK2. Protein concentration 0.5 per cent., Tris or acetate buffer, final  $\Gamma/2=0.15$ ,  $\square$  pH 7.5.  $\triangle$  pH 6.0.

*(c) The Relation between Ionic Strength and Zinc Binding*

It was found under the standard conditions of 0.5mM  $^{65}\text{Zn}$ , ionic strength 0.15 at pH 6.0 and 7.5, that the addition of sodium chloride up to a concentration of 0.85M ( $\Gamma/2=1.0$ ) did not affect the amount of zinc bound, although it is known to increase greatly the solubility of the zinc-protein complex.

*(d) The Relation between Protein Concentration and Zinc Binding*

This effect was studied at pH 7.5 with zinc concentrations of 0.5 and 8.5mM and with protein concentrations of 0.25, 0.50, and 1.00 per cent. It was found that the amount of zinc bound increased proportionally with the protein concentration at both zinc concentration levels.

*(e) Reversibility of Binding*

Each dialysis tube containing protein, protein-bound zinc, and free zinc acetate from experiments described in Section III (b) was wiped with filter paper and then re-dialysed against a fresh sample of the same buffer but without the addition of zinc. At the end of dialysis the concentration of radioactive zinc was measured in the dialysate and from this concentration the amount of

zinc bound to the protein under the new set of conditions calculated. Figure 3 shows that the binding at pH 7.5 is reversible over the range of zinc acetate concentrations studied. Similar results were obtained at pH 6.0, but the lower binding decreased the accuracy of the results.

(f) *Removal of Zinc from the Protein*

(i) *By Dialysis against Tap Water.*—When the contents of dialysis tubes derived from experiments under Section III (b) were dialysed against running tap water, the reversibility of binding was once again evident. It appears, however, that while 80 per cent. of the internal  $^{65}\text{Zn}$  was readily dialysed out in the first 2 days, the remaining 20 per cent. or so required 10 or more days for complete removal (Fig. 4). By contrast, in the absence of protein all the zinc dialysed out within 36 hr.

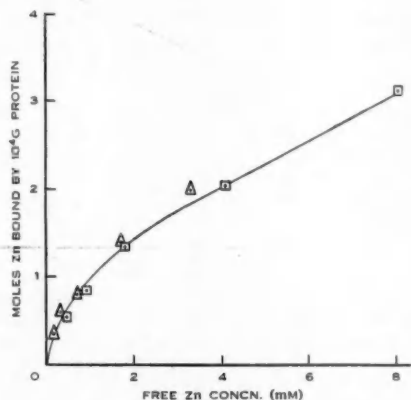


Fig. 3.—Reversibility of zinc binding by SCMK2 at various zinc concentrations. Protein concentration 0.5 per cent., Tris buffer pH 7.5, final  $\Gamma/2=0.15$ . □ Zinc binding after first equilibration. Δ Zinc binding after back dialysis.

(ii) *By Treatment with Chelating Agents and Dialysis against Tap Water.*—

Sodium citrate or Versene (ethylenediaminetetra-acetic acid disodium salt) was added to the contents of the dialysis tubes in a tenfold molar excess of the zinc present, and the pH adjusted to 6.0. After 24 hr dialysis against tap water, it was found that three times as much  $^{65}\text{Zn}$  had been removed from the protein solution in the presence of a chelating agent as in its absence. The addition of chelating agents did not however speed up the slower second phase of zinc release, corresponding to removal of the last 20 per cent. of internal zinc.

(g) *Comparison of SCMK2 Fractions*

The ability of the two SCMK2 fractions (P1, S1) to bind zinc was measured at pH 6.0 and 7.5 and at 0.5 and 10mM zinc acetate concentration. When the binding measurements were calculated to the same weight of protein it was

found that the S1 fraction bound about 75 per cent. of the amount of zinc bound by the P1 fraction. This is in contrast to the very great difference in solubility between the zinc complexes of the two fractions.

The bulk of bound zinc could be equally readily removed from the two fractions, but the remnants were removed more easily from the S1 than from the P1 fraction.

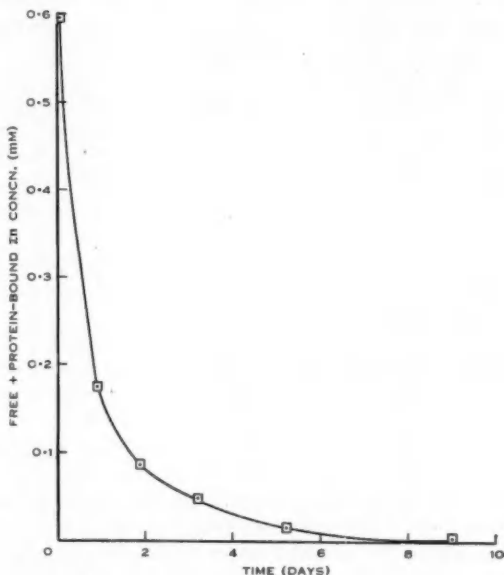


Fig. 4.—Removal of zinc from SCM2 by dialysis against tap water. Protein concentration 0.5 per cent., initial conditions were: zinc concentration 1.0mM, acetate buffer pH 6.0,  $\Gamma/2=0.15$ .

#### IV. DISCUSSION

The amount of zinc bound by SCM2 was found to be a function of the free zinc concentration (Fig. 2) and did not reach a maximum value over the range studied. When the results obtained at each pH are plotted as the reciprocal of the moles of zinc bound per mole of SCM2 against the reciprocal of the free zinc concentration, curves rather than straight lines are obtained. It is not possible from this data to extrapolate and thus calculate the maximum amount of zinc bound by the protein.

The extent of binding is usually calculated as the number of molecules of ligand bound by 1 g-molecule of protein. However, the molecular weight of SCM2 is not known with certainty, for Harrap (1957) found the surface mean molecular weight to be near 8000, while O'Donnell and Woods (1956b) with the ultracentrifuge showed that in solution there was a wide distribution

of molecular sizes with a mean value near 200,000 at pH 6.7. Therefore, in the present study an arbitrary value of 10,000 has been used.

According to Simmonds (1955), the protein contains only about 0.5 histidine residue per 10,000 g and thus more zinc is bound (Fig. 2) than can be accounted for by histidine binding alone, assuming a 1:1 zinc-histidine ratio (Gurd and Goodman 1952; Gurd 1954a). The reason for this is not known, but it may be related to the unfolded state of the protein (O'Donnell and Woods 1956b) exposing other groups which may bind zinc. Gurd (1954a, 1954b) reported that human plasma albumin had an increased affinity for zinc following certain types of denaturation, and suggested that the more random arrangement of the denatured protein might allow chelation with groups which had been brought into positions where they could react. However, this may not necessarily be the correct reason, for SCMK2 differs from native proteins in containing the modified amino acid residue *S*-carboxymethyl cysteine, and this may have some bearing on the amount of zinc bound. It is of interest to note that the difference between the amount of zinc bound at pH 6.0 and 7.5 (Fig. 2) in the 2 to 10mM free zinc concentration range roughly corresponds to the histidine content of the protein. Tanford, Swanson, and Shore (1955) and Tanford and Wagner (1954) state that the pK of the imidazole group in bovine plasma albumin is at pH 6.9, and in lysozyme between 6.5 and 7.0. This is about the middle of the range over which the increase in the zinc binding of SCMK2 corresponds to the histidine content, and it seems likely that it is the un-ionized form of histidine which binds zinc.

The difference in affinity of the zinc for the S1 and P1 fractions may be related to their differing histidine contents (0.78 and 1.19 histidine-N as percentage of total-N respectively according to Simmonds, unpublished data). However, the very great difference in solubility of the zinc complexes of these two proteins is probably due to other factors influencing solubility rather than to differences in the amount of zinc bound.

The concentration of zinc required for maximum precipitation of the protein at pH 6.0 (8 to 10mM) (Gillespie 1957) corresponds to about three atoms of zinc bound per 10,000 g of protein. The minimum solubility observed for the zinc-protein complex over the pH range 6 to 7 is not directly related to the amount of zinc bound, but is probably a reflexion of a changed pH-solubility relationship, as observed previously with the zinc complex of human plasma albumin (Cohn *et al.* 1950), and discussed by Gurd (1954b).

Since changes in ionic strength from 0.15 to 1.0 did not alter the amount of zinc bound, the effect of salt in making the zinc complex more soluble is probably due to its salting-in effect.

The removal of zinc from a zinc-protein complex by dialysis against water alone was rather slow (Fig. 4). The results indicate that about 80 per cent. of the total zinc, including both that free and protein-bound, was removed in 2 days, but the remainder of the zinc required upwards of 10 days for complete removal. Cunningham, Fischer, and Vestling (1955), working with insulin, pointed out that one portion of the zinc was more firmly bound than the remainder and could not be removed by dialysis except at an acid pH (pH 3.75). The



insolubility of SCMK2 under such conditions made it impossible to repeat these experiments with the wool protein.

The complete removal of zinc from the SCMK2 fractions is desirable before further physicochemical studies are undertaken. The present study shows this can best be achieved by treatment with chelating agents such as citrate, followed by prolonged dialysis against water, particularly in the case of the P1 fraction.

It appears that zinc is bound much more loosely to SCMK2 than to other proteins such as insulin. The data of Cunningham, Fischer, and Vestling (1955) show that insulin binds about 2.1 moles of zinc per 10,000 g of protein at a free zinc concentration of 0.24mM at pH 7.3, whereas SCMK2 for similar binding required a free zinc concentration of about 4.4mM. The loose binding of most of the zinc is also reflected in the ease with which the P1-zinc complex dissolves on repeated washing with water.

#### V. ACKNOWLEDGMENT

The authors wish to thank Miss B. F. Greening for technical assistance.

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## THE CHEMISTRY OF ANTS

### II. STRUCTURE AND CONFIGURATION OF IRIDOLACTONE (ISOIRIDOMYRMECIN)

By G. W. K. CAVILL\* and H. D. LOCKSLEY\*

[Manuscript received March 25, 1957]

#### Summary

Iridolactone, isolated from *Iridomyrmex nitidus* Mayr., is shown to be the lactone of  $\alpha$ -(2-hydroxymethyl-3-methylcyclopentyl)propionic acid and is identical with isoiridomyrmecin. Structural and configurational relationships of iridomyrmecin and of isoiridomyrmecin with the nepetalinic acids are discussed.

#### I. INTRODUCTION

The isolation and characterization of various terpenoid extractives from *Iridomyrmex* species of ants has been reported in Part I of this series (Cavill, Ford, and Locksley 1956a). Iridomyrmecin, originally isolated in Italy (cf. Pavan 1955), has been the subject of several papers (Fusco, Trave, and Vercellone 1955a, 1955b) whilst the structures of iridodial and iridolactone have been reported in a preliminary note (Cavill, Ford, and Locksley 1956b). The chemistry of iridolactone is now considered in more detail and its relationship with iridomyrmecin discussed.

### II. STRUCTURE OF IRIDOLACTONE (isoIRIDOMYRMECIN)

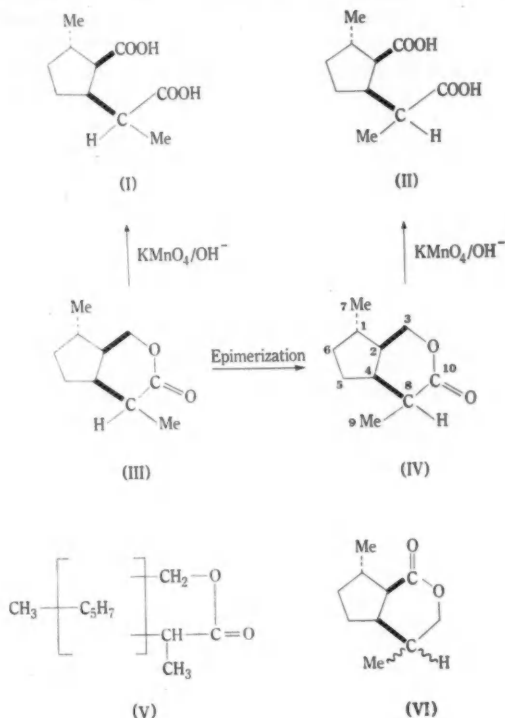
Iridolactone,  $C_{10}H_{16}O_2$ , m.p. 58–59 °C,  $[\alpha]_D^{17} -62^\circ$ , isolated from *I. nitidus* and characterized as the hydrazide (cf. Part I of this series), has now been converted into the parent hydroxy acid,  $C_{10}H_{18}O_3$ . The ready precipitation of this acid from aqueous solution, at pH 4, has assisted in the isolation and purification of iridolactone, particularly when mixed with stereoisomers (Ford, personal communication). On standing, the hydroxy acid partly reverts to iridolactone and some polymeric material is formed. The lactone is regenerated on distillation of the hydroxy acid, or the hydrazide, under reduced pressure.

As iridolactone did not absorb hydrogen in the presence of a palladium-charcoal catalyst and gave no colour with tetranitromethane, a carbocyclic ring is indicated, in addition to the lactone ring. Reduction of the lactone with lithium aluminium hydride gave iridodiol,  $C_{10}H_{20}O_2$ , characterized as the bis-*p*-nitrobenzoate. Iridodiol gave no colour with tetranitromethane.

Oxidation of iridolactone with alkaline potassium permanganate solution, under controlled conditions, gave an almost quantitative yield of a dicarboxylic acid,  $C_{10}H_{16}O_4$ , m.p. 81–82 °C,  $[\alpha]_D^{25} +24^\circ$ , and demonstrated the presence of the  $-\text{CH}_2-\text{O}-\text{CO}-$  group. A comparable oxidation of iridomyrmecin

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gave the dicarboxylic acid, m.p. 117–118 °C,  $[\alpha]_D^{22} +14^\circ$ , previously obtained by Fusco, Trave, and Vercellone (1955a). The determination of the structure and configuration of the nepetalinic acids (McElvain and Eisenbraun 1955) has materially assisted in the elucidation of the structure of iridomyrmecin. Following upon an initial suggestion by Professor D. H. R. Barton, Fusco,



For structures I–VI the following should be noted:

(a) Implications of the numbering system adopted here (see IV) will be discussed in a later paper.

(b) Professor S. M. McElvain has recently advised us of a revision of configuration at  $C_2$  in the nepetalinic acids (I and II). The new configuration is adopted in the present paper (cf. McElvain and Eisenbraun 1955).

(c) The configuration at  $C_8$  in structures I and III is opposite to that in II and IV.

Trave, and Vercellone (1955b) have shown that the di-acid, m.p. 117–118 °C, from the oxidation of iridomyrmecin is identical with the nepetalinic acid (I). Hence they have replaced their partial structure V for iridomyrmecin by III. Similarly our di-acid, m.p. 81–82 °C, from oxidation of iridolactone is identical with the nepetalinic acid (II).

Fusco, Trave, and Vercellone (1955a) have interpreted their conversion of iridomyrmecin into *isoiridomyrmecin*, by the action of potassium methoxide solution, as an epimerization of the asymmetric centre adjacent to the lactone carbonyl group (see III and IV). *isoIridomyrmecin* should thus give nepetalinic acid (II) on oxidation and iridolactone could be identical with *isoiridomyrmecin*, for which Fusco, Trave, and Vercellone (1955a) report m.p. 56.5–57 °C,  $[\alpha]_D^{20}$  –52.5°. Alternatively, iridolactone could have structure VI and be the epimer which yields the nepetalinic acid (II) on oxidation. We have also epimerized iridomyrmecin (III), achieving an 83 per cent. conversion into *isoiridomyrmecin* (IV), m.p. 56–57 °C,  $[\alpha]_D^{24}$  –59°. This compound and the specimen kindly supplied by Professor Fusco do not depress the m.p. of iridolactone, which is therefore represented by IV. The name iridolactone which has described the naturally occurring compound is now replaced by *isoiridomyrmecin*.

A polarimetric study (see Table 1) of the epimerization of *isoiridomyrmecin*, with sodium ethoxide in absolute ethanol, indicates a complex reaction. However, this equilibration gives a 14 per cent. conversion into iridomyrmecin, and complements the 83 per cent. conversion of iridomyrmecin into *isoiridomyrmecin*. Anhydrous potassium carbonate in boiling xylene, a reagent previously employed for the epimerization of the methyl substituent (adjacent to the lactone carbonyl group) in santonin derivatives (cf. Cocker, Cross, and Lipman 1949), also converts iridomyrmecin into *isoiridomyrmecin*, but the small scale of our experiments did not allow the equilibrium to be determined accurately.

It cannot be decided on the above evidence, whether the alkaline epimerizations have taken place with, or without, rupture of the lactone ring. Acid conditions would eliminate the possibility of the lactone ring opening, and should give more definite information on the reaction: unfortunately, no variation in the specific rotation occurred during the attempted epimerization of each of these ant products in hot formic acid.

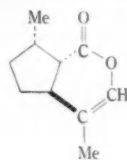
The infra-red spectra of iridomyrmecin and *isoiridomyrmecin* (see Section IV) show the frequency of the lactone carbonyl groups at 1758 and 1761  $\text{cm}^{-1}$  respectively. These values are higher than normal for  $\delta$ -lactones (cf. Cole 1954) and indicate slight strain, which is attributed to the fusion of the more rigid *cyclopentane* nucleus to the  $\delta$ -lactone ring.

### III. CONFIGURATION OF IRIDOMYRMECIN AND *isoIRIDOMYRMECIN*

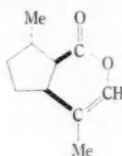
The absolute configuration of the substituents at the asymmetric centres of the *cyclopentane* nucleus in iridomyrmecin follows from the elucidation of the stereochemistry of nepetalactone and the nepetalinic acids. Previous work (see Eisenbraun and McElvain 1955; McElvain and Eisenbraun 1955) had indicated a *trans*-junction of the *cyclopentane* and lactone rings (cf. structure VII); however, more recent studies (McElvain, personal communication) have shown that this junction is *cis*, and nepetalactone is now represented as VIII.

Hence iridomyrmecin and *isoiridomyrmecin*, which differ in configuration at C<sub>8</sub>, are represented by structures IX and X, or vice versa. Two conformational isomers (IXa and IXb, and Xa and Xb) are theoretically possible for

each of these structures, but a conformational analysis indicates that the ant lactones are most likely to be represented by those isomers (IXa and Xb), in which the methyl group at C<sub>8</sub> is in an equatorial position.

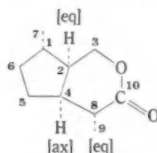


(VII)

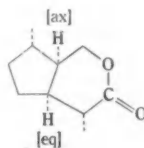


(VIII)

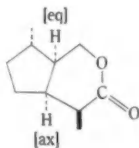
Other approaches to the problem of the configuration at C<sub>8</sub> in iridomyrmecin and *isoiridomyrmecin* are being examined.



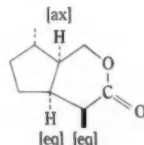
(IXa)



(IXb)



(Xa)



(Xb)

#### IV. EXPERIMENTAL

Melting points are uncorrected. Light petroleum has b.p. 40–60 °C. All specific rotations are measured in a 2-dm tube. Alumina refers to alumina oxide, Peter Spence, grade H. Neutralized alumina is prepared by washing grade H alumina with methanol-acetic acid (9:1), triturating with hot methanol until all washings are neutral, and drying (oven) at 150–200 °C. Carbon, hydrogen, and nitrogen microanalyses are by Dr. E. Challen and Mr. D. Weeden, and infra-red spectra by Mr. I. Reece, of this University.

(a) *The Hydroxy Acid*.—Iridolactone (1.1 g) was dissolved in aqueous potassium hydroxide (15 ml; 2N) and the solution cooled in ice. The *hydroxy acid* (0.35 g) which rapidly crystallized from solution on addition of acetic acid (12 ml; 8N), was filtered off and finally obtained as colourless needles, m.p. 110–112 °C (decomp.), from aqueous ethanol (Found: C, 64.6; H, 9.8%. Calc. for C<sub>10</sub>H<sub>14</sub>O<sub>3</sub>: C, 64.5; H, 9.7%). Ether extraction of the filtrate (acidified with dil. hydrochloric acid to pH 1) gave iridolactone (0.55 g), which yielded a further quantity of the hydroxy acid on repetition of the above procedure. The hydroxy acid (40 mg), on sublimation at 130 °C/0.1 mm gave iridolactone (30 mg), m.p. 47–50 °C,  $[\alpha]_D^{17}$  –51°, recrystallized from light petroleum at low temperature, m.p. and mixed m.p. 58–59 °C.

(b) *Reduction of Iridolactone*.—(i) Iridolactone (95 mg) in ethanol (15 ml) with chloroform (0.1 ml) was hydrogenated in the presence of a palladium catalyst (10% Pd/C). No hydrogen was absorbed after 2 hr.

(ii) Lithium aluminium hydride (170 mg) in ether (40 ml) was slowly added to iridolactone (120 mg) in ether (30 ml) and the mixture refluxed for 1 hr. Excess lithium aluminium hydride was removed with ethyl acetate (1 ml, in ether) and the complex decomposed with ice (10 g) and dilute sulphuric acid (3 ml; 2N). The ether layer, after shaking with saturated sodium hydrogen carbonate solution, yielded an oil (150 mg) which slowly crystallized. *Iridodiol*, further purified by chromatography on neutralized alumina (eluted with benzene-chloroform, 1:1), was finally isolated as colourless needles (110 mg), m.p. 76–77 °C,  $[\alpha]_D^{25} + 6.4^\circ$  (c, 1.179 in chloroform) from carbon tetrachloride (Found: C, 69.7; H, 11.8%. Calc. for  $C_{10}H_{20}O_2$ : C, 69.7; H, 11.7%).

(iii) *Iridodiol Bis-p-nitrobenzoate*.—The substance was prepared, in the usual manner, from iridodiol (40 mg) and *p*-nitrobenzoyl chloride (780 mg) in anhydrous pyridine (1 ml). The ester, purified by chromatography on neutralized alumina (eluted with benzene), crystallized as pale yellow prisms (60 mg), m.p. 99–100 °C, from light petroleum (Found: C, 61.5; H, 5.6; N, 6.2%. Calc. for  $C_{24}H_{28}O_8N_2$ : C, 61.3; H, 5.6; N, 6.0%).

(c) *Potassium Permanganate Oxidations*.—(i) Potassium permanganate (12 ml; 5% aqueous soln.) was added to iridolactone (240 mg) in potassium hydroxide solution (0.3 g in 10 ml of water) and the mixture allowed to stand for 2 days at room temperature. The precipitated manganese dioxide was filtered and washed. The filtrate, after acidification and reduction of excess permanganate with sodium hydrogen sulphite, was extracted with ether (5 × 20 ml). The ethereal layer, then extracted with sodium hydrogen carbonate solution, did not contain any neutral material. The alkaline layer yielded a viscous acidic oil (250 mg, crude) which solidified overnight. Portion of the crude acid (0.14 g) was purified via the barium salt to give *iridodicarboxylic acid*, isolated as colourless prisms (71 mg), m.p. 81–82 °C,  $[\alpha]_D^{25} + 24^\circ$  (c, 0.707 in chloroform) from light petroleum at low temperature (Found: C, 60.0; H, 8.2%; equiv. wt. (titn.), 105. Calc. for  $C_{18}H_{16}O_4$ : C, 60.0; H, 8.0%; equiv. wt., 100). A mixed m.p. with nepetalinic acid, m.p. 85 °C,  $[\alpha]_D^{25} + 30.2^\circ$ , was undepressed (m.p. 81–83 °C). The infra-red spectra (run as a "Nujol" mull) were indistinguishable.

Other oxidations of iridolactone at higher temperatures, 50 and 90–100 °C, were unsuccessful and most of the iridolactone was recovered.

(ii) *Iridomyrmecin* (150 mg) in potassium hydroxide solution (0.2 g in 10 ml of water) was treated with potassium permanganate (8 ml; 5% aqueous solution) and the mixture allowed to stand at room temperature for 3 days. The reaction, worked up as above, gave an acidic fraction (70 mg). The di-acid, purified via the lead salt, was isolated as colourless prisms (60 mg), m.p. 117–118 °C,  $[\alpha]_D^{22} + 14^\circ$  (c, 0.593 in chloroform) from light petroleum-ether (Found: C, 59.8; H, 7.9%. Calc. for  $C_{10}H_{16}O_4$ : C, 60.0; H, 8.0%).

(d) *Conversion of Iridomyrmecin into isoIridomyrmecin*.—Iridomyrmecin (500 mg,  $[\alpha]_D^{25} + 210^\circ$  (c, 0.976 in carbon tetrachloride)) in absolute methanol (6 ml, purified via magnesium methoxide (Vogel 1951)) was added to sodium methoxide in absolute methanol (prepared from sodium (1 g) in methanol (22 ml)). After refluxing the solution for 2 hr the methanol was removed under reduced pressure. Ether extraction (6 × 10 ml) of the residue, after acidification, gave a viscous oil (480 ml) which slowly crystallized.

The product was recrystallized from light petroleum at low temperature to yield *isoiridomyrmecin*, m.p. 56–57 °C,  $[\alpha]_D^{24} - 59^\circ$  (c, 0.562 in carbon tetrachloride). Mixed m.p.'s were undepressed with a specimen of *isoiridomyrmecin*, kindly supplied by Professor Fusco, and with iridolactone, from *I. nitidus*. The infra-red spectra of iridolactone and *isoiridomyrmecin* were indistinguishable.

(e) *Epimerization Reactions*.—Iridomyrmecin had  $[\alpha]_D^{25} + 210^\circ$  (c, 0.976 in carbon tetrachloride) and the infra-red absorption spectrum, in carbon tetrachloride showed bands at 2942, 2907, 2858, 1758, 1476, 1458, 1449, 1381, 1377, 1358, 1331, 1325, 1306, 1279, 1176, 1155, 1132,

1073, and  $941\text{ cm}^{-1}$ . *iso*Iridomyrmecin had  $[\alpha]_D^{17} -62^\circ$  (c, 1.009 in carbon tetrachloride) and the infra-red absorption spectrum, in carbon tetrachloride, showed bands at 2941, 2920, 2872, 1761, 1478, 1457, 1381, 1350, 1327, 1168, 1151, 1129, 1055, 1036, and  $933\text{ cm}^{-1}$ .

(i) Iridomyrmecin (110 mg) was epimerized with methanolic sodium methoxide (sodium (30 mg) in absolute methanol (50 ml)) as above. After 1 hr, the solution was cooled and an aliquot (10 ml) removed. This aliquot, worked up as above, gave a crystalline residue,  $[\alpha]_D^{22} -12^\circ$ . The specific rotation of the lactone mixture from subsequent aliquots was unchanged,  $[\alpha]_D^{22} -17^\circ$ , and represents an 83% conversion into *iso*iridomyrmecin.

(ii) *iso*Iridomyrmecin (107 mg) was treated with sodium ethoxide in absolute ethanol (from sodium (22 mg) in ethanol (15 ml)) and the solution immediately transferred to a polarimeter tube. The rotation (see Table I) finally reached a constant value.

TABLE I

Time (min)	Specific Rotation at $16^\circ\text{C}$	Time (min)	Specific Rotation at $16^\circ\text{C}$
0	-13	144	33
4	-3	179	29
5	-1	219	25
6.5	3	279	20
9	13	320	17
13	22	342	16
18	28	424	12
23	34	435	12
28	38	512	8
33	40	582	6
39	42	1320	-3

The residue, after removal of ethanol under reduced pressure, was acidified with dilute hydrochloric acid and extracted with ether. The product, after distillation under reduced pressure, had  $[\alpha]_D^{24} -23^\circ$  (c, 0.637 in carbon tetrachloride), and on recrystallization gave *iso*iridomyrmecin, m.p. and mixed m.p.  $57-58^\circ\text{C}$ , from light petroleum at low temperature. Assuming *iso*iridomyrmecin and iridomyrmecin to be present, the above specific rotation corresponds to a 14% conversion into iridomyrmecin.

(iii) Iridomyrmecin (56 mg) was added to potassium carbonate (200 mg) in xylene (5 ml) and the mixture gently refluxed for 10 hr. (Xylene, purified by twice distilling sulphur-free xylene from sodium, had b.p.  $138-140^\circ\text{C}$ . Potassium carbonate (AnalaR) was finely ground and heated at  $350^\circ\text{C}$  (oven) for  $1\frac{1}{2}$  hr prior to use.) On cooling, the potassium carbonate was filtered and washed with xylene (10 ml). The residue (50 mg), obtained after removal of xylene, was distilled under reduced pressure to give an oil (42 mg),  $[\alpha]_D^{17} +81^\circ$  (c, 0.419 in carbon tetrachloride). The distinct odour of *iso*iridomyrmecin was evident. The infra-red spectrum of the product possessed bands at  $1055$  and  $1036\text{ cm}^{-1}$  which are characteristic of *iso*iridomyrmecin.

Similarly, *iso*iridomyrmecin (280 mg) was refluxed with anhydrous potassium carbonate (800 mg) in xylene (12 ml) for 10 hr. The product, worked-up as above, had  $[\alpha]_D^{18} -43^\circ$  (c, 2.638 in carbon tetrachloride).

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## SHORT COMMUNICATIONS

### CALCULATION OF PARTIAL MOLAR VOLUME CHANGES AT HIGH PRESSURES\*

By W. STRAUSS†

Buchanan and Hamann (1953) and Hamann and Strauss (1955, 1956) have suggested that the increase in ionization of weak electrolytes with increasing pressure is caused by a lowering of the solvation-free energy of their ions. This change can be theoretically estimated (Hamann and Strauss 1955) from the Born equation for solvation energy (Born 1920), which expresses the free energy of solvation  $\Delta\bar{G}$  as a function of two quantities which vary with pressure; the dielectric constant of the solvent  $D_p$ , and the radius of the ions  $r_p$ . For a mole of singly charged ions at the pressure  $p$ ,  $\Delta\bar{G}$  is given by

$$\Delta\bar{G} = -\frac{N\epsilon^2}{2r_p} \left(1 - \frac{1}{D_p}\right), \dots\dots\dots (1)$$

where  $N$  is Avogadro's number and  $\epsilon$  is the electronic charge.

In the present paper the calculations are extended to the changes in volume which accompany the development of ionic charges in solutions at high pressures. The theoretical partial molar volume change for the solvation of a mole of ions can be calculated by differentiating the Born equation with respect to pressure:

$$\begin{aligned} \Delta\bar{V} &= \left(\frac{\partial\Delta\bar{G}}{\partial p}\right)_T \\ &= \frac{N\epsilon^2}{2} \left(1 - \frac{1}{D_p}\right) \frac{1}{r_p^2} \left(\frac{\partial r_p}{\partial p}\right)_T - \frac{N\epsilon^2}{2r_p} \frac{1}{D_p^2} \left(\frac{\partial D_p}{\partial p}\right)_T. \dots\dots (2) \end{aligned}$$

In applying this formula at high pressures,  $D_p$  and  $(\partial D_p/\partial p)_T$  have been obtained from an empirical equation which Owen and Brinkley (1943) found satisfactory for a number of polar liquids to 12000 kg/cm<sup>2</sup>. The values of  $r_p$  and  $(\partial r_p/\partial p)_T$  have been estimated from the compressions of some alkali halide crystals (determined experimentally by Bridgman (1931)) assuming that the positive and negative ions are equally compressible.

Table 1 gives the calculated values of the partial molar volume of solvation of a typical ion pair  $\text{Cs}^+ + \text{F}^-$  in a number of liquids. The results for other

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TABLE 1  
THEORETICAL MOLAR VOLUME CHANGES FOR THE SOLVATION OF THE ION PAIR  $\text{Cs}^+ + \text{F}^-$  IN VARIOUS MEDIA AT 30 °C

Medium ( $\text{cm}^3 \text{mole}^{-1}$ )	Pressure ( $\text{kg/cm}^2$ )				
	1	100	250	500	1500
Water .. .. .	-19.7	-19.5	-19.1	-18.6	-17.0
Methanol .. ..	-42.1	-39.8	-36.9	-33.2	-25.3
Ethanol .. .. .	-53.8	-50.8	-47.0	-42.1	-31.2
Acetone .. .. .	-74.8	-67.7	-59.6	-50.4	-33.5
Bromobenzene ..	-118.2	-110.9	-101.5	-89.3	-61.7
	2500	4000	8000	12000	
Water .. .. .	-15.9	-14.6	-12.3	-10.5	
Methanol .. ..	-21.5	-18.3	-14.1	-11.6	
Ethanol .. .. .	-25.9	-21.5	-16.0	-12.9	
Acetone .. .. .	-26.7	-21.6	-15.8	-12.7	
Bromobenzene ..	-48.3	-37.3	-24.7	-18.9	

alkali halides are substantially the same. The theoretical volumes of solvation in water and methanol listed in Table 1 are compared with the experimental

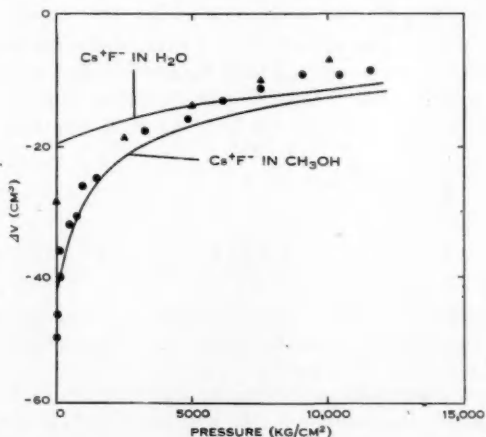


Fig. 1.—Comparison of theoretical and experimental partial molar volume changes in water and methanol to pressures of 12,000  $\text{kg/cm}^2$ .

▲  $\text{NH}_3$  in  $\text{H}_2\text{O}$ . ● Piperidine in  $\text{CH}_3\text{OH}$ .

partial molar volume changes for the ionization of ammonia in water (Hamann and Strauss 1955) and of piperidine in methanol (Hamann and Strauss 1956); see Figure 1. The good agreement of the trends of the calculated and experi-

mental changes shows that the behaviour of the partial molar volume changes in the two solvents can be explained by the effect of pressure on the radii of the ions and the dielectric constants of the media.

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## INFRA-RED ABSORPTION SPECTRA OF METAL HYPONITRITES\*

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R. L. WERNER<sup>‡</sup>

In pursuance of the objective towards which the papers of Le Fèvre, O'Dwyer, and Werner (1953), Le Fèvre, Sousa, and Werner (1956), and Le Fèvre and Werner (1957) have been directed, we commenced, 2 years ago, an infra-red spectrographic study of salts of hyponitrous acid. Some six of these had been surveyed between 4000 and 650  $\text{cm}^{-1}$  when a report appeared from Kuhn and Lippincott (1956) on three of the salts under examination by us. Since, in main essentials, their results and ours are in agreement, the purpose of this communication is to record our observations for the hyponitrites of lead, magnesium, barium, and cobalt for which data have not previously been published.

### Experimental

*The Preparation of Hyponitrites.*—Available methods may be classified into two major groups: (i) those which use compounds whose molecules each contain one atom of nitrogen, and (ii) those which start from substances having two or more atoms of nitrogen in their molecules. Under (i) fall all the procedures involving the reduction of nitrates, nitrites, or nitric oxide, and the direct or indirect oxidation of hydroxylamine; under (ii) come reactions between nitrous acid and hydroxylamine (or its derivatives). References may be found in Mellor's "Comprehensive Treatise", Vol. 8, p. 413.

At the beginning of our work several of the type (i) processes were tried; difficulty was experienced in obtaining specimens free from carbonate, nitrite,

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etc. (revealed by spectroscopic examination). The modification of Divers' original reduction of sodium nitrite (by sodium amalgam and water), due to Addison, Gamlen, and Thompson (1952), was successful, but tedious compared with the addition of alkyl nitrites to an alcoholic solution of hydroxylamine and sodium ethylate (Jones and Scott 1924; Scott 1927); the last method was that finally adopted for sodium hyponitrite, from which in turn other hyponitrites were formed by double decompositions.

Running a calculated amount of 5 per cent. aqueous silver nitrate, acidified slightly with nitric acid, into a cold dilute solution of sodium hyponitrite in water, gave the yellow insoluble silver salt as a precipitate. It was collected, washed with water followed by a little ethanol and ether, and dried to constant

TABLE 1

INFRA-RED ABSORPTION FREQUENCIES (AS  $\text{CM}^{-1}$ ) NOTED FOR FOUR HYPONITRITES  
Relative intensities throughout any one spectrum indicated by numbers 1-10;  
b, broad; Sh, shoulder; upper section of table shows results with NaCl prism,  
lower with KBr prism

$\text{PbN}_2\text{O}_2$	$\text{BaN}_2\text{O}_2$	$\text{CoN}_2\text{O}_2$	$\text{MgN}_2\text{O}_2$
1128 (1)b	1157 (1) 1035 (6) 1015 (7) 1006 (7)	1151 (1) 1050 (6)b	1151 (1) 1051 (6)
990 (7)	996 (7) 870 (1) 858 (3)	896 (1)	862 (2)
689 (1)Sh 680 (3)	691 (1)		
683 (5) 652 (1)Sh 589 (2) 515 (4)b	696 (2)   515 (8) 420 (4)b	670 (3)b 600 (1)Sh  577 (1) 452 (2) 441 (2)	585 (6)b 470 (5)b

weight over phosphoric oxide in an opaque vacuum desiccator. Silver hyponitrite, dissolved in ammonium hydroxide, treated with aqueous barium nitrate gave barium hyponitrite at once; after filtration and washing (water, ethanol, ether) it was dried and stored in a vacuum (phosphoric oxide). The magnesium, cobalt, and lead salts were obtained directly from sodium hyponitrite in water by interaction with solutions of magnesium chloride, cobalt chloride, and lead acetate respectively.

*Infra-Red Spectra.*—Mulls in "Nujol" and hexachlorobutadiene were examined from *c.* 4000 to  $400\text{ cm}^{-1}$ , using rock-salt and potassium bromide prisms. Absorptions due to the hyponitrites are presented in Table 1.

*Discussion*

The spectra show no notable features above *c.* 1160  $\text{cm}^{-1}$ . This fact indicates that our specimens were free from the most likely impurities viz. carbonates, nitrites, and nitrates. Miller and Wilkins (1952) included a number of these salts among the 159 studied by them; they reported the following absorptions ( $\text{cm}^{-1}$ ), each labelled "very strong":

$\text{Na}_2\text{CO}_3$	1440	$\text{NaNO}_3$	1358	$\text{NaNO}_2$	1250
$\text{K}_2\text{CO}_3$	1450	$\text{KNO}_3$	1380	$\text{KNO}_2$	1235
$\text{BaCO}_3$	1440	$\text{AgNO}_3$	1348	$\text{Ba}(\text{NO}_2)_2$	1235
$\text{CoCO}_3$	1450				

None of these bands is displayed to any extent on our records. Specimens deliberately contaminated with carbonates showed definite absorption\* at 1440–1450  $\text{cm}^{-1}$ .

Hyponitrites thus lack spectral analogies with either metal nitrites or nitrates. Miller and Wilkins list no bands for  $\text{NaNO}_2$  or  $\text{KNO}_2$  between 1650 and 1750  $\text{cm}^{-1}$ , for  $\text{Ba}(\text{NO}_2)_2$  a "medium" absorption at 1640  $\text{cm}^{-1}$  is given. Among the nitrates, the sodium and potassium salts respectively absorb at 1790 and 1767  $\text{cm}^{-1}$ , both annotated "very weak", but silver nitrate is clear at this point. Neither nitrites nor nitrates have bands of any strength just above 1000  $\text{cm}^{-1}$ .

Comparison may also be made with organic nitrites and nitrosamines. The absorption maxima found by Haszeldine and Jander (1954) for examples of these classes can be grouped within limits as follows:

*Alkyl Nitrites*: 1739–1727 vs., 1647–1370 vs. to vvs., 810–787 s.br.

*Dialkylnitrosamines*: 1745–1680 vvw., 1662–1163 s. to vvs., 1090–1000 vs. to vvs.†

In the alkyl nitrites Haszeldine and Jander assign the highest frequency group to  $\text{N}=\text{O}$  stretching vibrations, and the lowest to the same mode for  $\text{N}-\text{O}$  (cf. Tarte 1952). The former of these is absent from the hyponitrite spectra. It is interesting to note that dimeric nitric oxide—a molecule which may have much the same structure and shape as the hyponitrite anion (however, cf. Dulmage, Meyers, and Lipscomb 1951)—exhibits strong infra-red absorptions at 1770 and 1863  $\text{cm}^{-1}$ , and Raman displacements at 1861 s. and 1760 w.  $\text{cm}^{-1}$  (Smith, Keller, and Johnston 1951); these can reasonably be related to others known for  $\text{N}=\text{O}$  in a number of well-established cases (e.g.  $\text{ClNO}$ , 1799,  $\text{BrNO}$ , 1801,  $\text{NO}$ , 1906  $\text{cm}^{-1}$ ). Such facts are consistent with hyponitrites not containing a  $-\text{N}=\text{O}$  group.

In the dialkylnitrosamines the strong bands at *c.* 1100  $\text{cm}^{-1}$  can be explained by resonance of the type  $\text{R}_2\text{N.N}=\text{O} \longleftrightarrow \text{R}_2\text{N}^+:\text{N}-\text{O}^-$  causing absorption at

\* The statement by Addison, Gamlen, and Thompson (1952) that it is "not possible by any qualitative test to detect the presence of carbonate in the hyponitrite" is therefore no longer valid.

† Strengths are as indicated by the original authors: s., strong; br., broad; v., very; w., weak.

points intermediate between those due to  $\text{N}=\text{O}$  and  $\text{N}-\text{O}$ . Since hyponitrites also show features in the  $1000\text{--}1200\text{ cm}^{-1}$  region, it is possible that they similarly possess nitrogen-oxygen double-single hybrid links, although the most obvious way of formulating this appears to violate the adjacent charge rule:



Instances where  $\nu_{\text{NO}}$  is *c.*  $1000\text{ cm}^{-1}$  include hydroxylamine (cited by Syrkin and Dyatkina 1950), *N*-nitroso-*ON*-bistrifluoromethylhydroxylamine (Jander and Haszeldine 1954), and the nitrosopentammine cobalt salts  $[(\text{NH}_3)_5\text{CoNO}]\text{X}_2$  (Milward, Wardlaw, and Way 1938; Short 1954). The last example well illustrates the sensitivity of  $\nu_{\text{NO}}$  to  $\text{N}-\text{O}$  bond type, the red nitrate or sulphate having bands at  $1047$  or  $1084\text{ cm}^{-1}$  respectively, in contrast to sodium nitroprusside in which  $\nu_{\text{NO}}$  is  $1925\text{ cm}^{-1}$ , the differences arising from the coordination of either  $(\text{N}=\text{O})^-$  or  $(\text{N}=\text{O})^+$  to the central metal atom.

Finally, we add that solutions of sodium hyponitrite in water have been examined in the Hilger E612 direct recording Raman spectrometer, each scanning taking about 20 min. Solutions were filtered under gravity through sintered glass of No. 4 pore size. The exciting light was Hg  $4358\text{ \AA}$ . Poor records were obtained (apparently due to the development of minute gas bubbles) showing peaks at *c.*  $1390$  and  $960\text{ cm}^{-1}$ . These agree with the results of Kuhn and Lippincott, obtained photographically after exposures of 1 to 2 hr.

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## IONIZED STATES OF MOLECULAR CRYSTALS\*

By L. E. LYONS†

The ionized electronic states (cf. Seitz 1940) expected in molecular crystals are of two types, in which (i) the electron is free within the crystal, and (ii) the electron is bound to an individual molecule.

(i) If the molecular orbital from which the electron is excited is large enough to encompass several neighbouring molecular sites then the ionization takes place in a medium having the bulk dielectric constant  $\epsilon$  (equal to the square of the refractive index). We assume an isotropic crystal although this restriction is easily removed. Ionization from such orbitals needs energy

$$I_c = I_g / \epsilon^2,$$

where  $I_g$  is the gaseous ionization potential (Mott and Gurney 1940). Excitation from such an orbital to a higher orbital is expected to give rise to Rydberg levels over a range calculated as 0.25 eV. Such levels have been reported in  $\text{Cu}_2\text{O}$  and  $\text{CdS}$  (Gross and Karryev 1952; Hayashi and Katsuki 1952) but have not yet been discovered in organic crystals.

If the original orbital is small compared to the intermolecular spacing, then  $I_g - I_c$  is due only to  $P$ , the polarization energy of the crystal. For anthracene,  $P$  has been calculated as 2 eV. Photoemission has been observed with anthracene (Carswell and Iredale 1953) irradiated with quanta of energy 5.6 eV, which compares with the value calculated as 6.2 eV.

(ii) Levels with the electron bound to a neutral molecule occur at lower energies than those for which the electron is free, provided the molecule has a positive electron affinity  $A$ . For anthracene,  $A = 1.4$  eV (Lyons 1950). Polarization when the electron is on the nearest neighbour to the positive hole has been calculated as 0.8 eV. The mutual attraction of the opposite charges lowers the ionization energy by 2.8 eV for nearest neighbours. The net energy needed to form the lowest ionized state is accordingly 2.2 eV (cf. von Hippel 1936).

There will be many ionized levels between that of lowest energy and the point  $I_c - A$  at which the positive and negative centres are separated to a large distance within the crystal.

Consequently, the energy diagram expected for anthracene will be in outline similar to Figure 1, in which for simplicity excitation transfer is neglected. This neglect is not as serious as might at first seem, provided attention is confined to optically allowed transitions.

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It is seen that the lowest ionized states are comparable in energy to the usual  $2p\pi$  excited states. Transitions to the ionized states are expected to be very feeble due to the small overlap of the orbitals of different molecules. Even for nearest neighbours the oscillator strength is estimated as  $10^{-5}$  to  $10^{-6}$ , little greater than that of singlet-triplet transitions.

The observation in both absorption (Prikhotjko 1944; McClure and Schnepf 1955) and fluorescence (Obreimov and Shabaladas 1943) of a band in an *c.* 3 mm thick naphthalene crystal at  $29945\text{ cm}^{-1}$  is possibly a direct observation of an ionized state.

Photoconduction in molecular crystals is expected if an ionized bound-electron state produced optically is then dissociated (e.g. thermally or electrically). The positive and negative centres would then be free to move through the crystal independently and so contribute to the conductivity. This is indeed what is observed (Putseiko 1949; Lyons and Morris 1957).

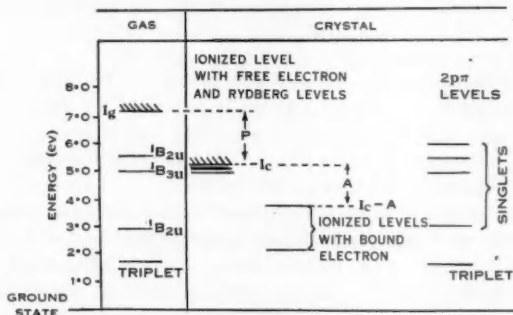


Fig. 1.—Some energy levels in anthracene.

The positive temperature coefficient of photoconduction (Chynoweth and Schneider 1954; Bree and Lyons 1956) becomes explicable for this mechanism as due to the energy necessary to dissociate the ion pair.

The existence in these crystals of positive and negative ions has been suggested earlier (Lyons and Morris 1957), to explain the occurrence of observed space charge effects. Details of the present calculations will be published elsewhere. Use of a von Hippel cycle in the case of helium, but without numerical values of the inclusion of polarization terms has been made independently by Dr. J. N. Murrell, with whom, as with Professor William Moffitt, I have had interesting discussions.

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## A CARBONATO COMPLEX OF MOLYBDENUM $K_6Mo(CO_3)_5 \cdot 2H_2O$ \*

By M. C. STEELE†

Mellor (1948, p. 659) states that no molybdenum carbonate has been reported and there appears to be nothing in more recent literature.

The carbonato complex reported in the present paper was formed when an attempt was made to produce an iodo complex with molybdenum(III).

### Experimental

Potassium molybdate solution was made acid with hydriodic acid and about 2 g of potassium iodide added. This solution was electrolysed using a mercury cathode and a carbon anode. The iodine liberated, markedly corroded the carbon anode and a carbon deposit formed which was filtered off. The carbon anode was replaced by a platinum anode and electrolysis was continued. The final reduced solution was a very light brown-red colour which was quite different from the more intense red coloured solutions of molybdenum(III), chloride or bromide.

The reduced solution was evaporated under suction at 70° C to about 50 ml; ethanol was added; two layers formed, the electrolysed solution and the ethanol layer. Carbon dioxide was bubbled through the reduced electrolyte and a white precipitate formed from the aqueous layer. The precipitate was filtered, washed with ethanol, and dried at 100° C (Found: Mo, 14.7;  $CO_3$ , 45.0; K, 35.4%). This is in agreement with  $K_6Mo(CO_3)_5 \cdot 2H_2O$  or  $K_4Mo(CO_3)_4 \cdot K_2CO_3 \cdot 2H_2O$ .

The molecular conductivity of M/1016 at 25° C = 680 mhos. The conductivity increases slightly with time indicating that the compound undergoes some hydrolysis.

Magnetic susceptibility measurements showed this compound to be diamagnetic ( $\chi \times 10^6 = -0.052$ ) involving Mo(IV).

Heide and Hofmann (1896) reduced an acid solution of molybdenum trioxide with potassium iodide. The excess iodine was removed by electrolysis. To this

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solution they added potassium cyanide to obtain red crystals of the red cyanide to which they assigned the formula  $4\text{KCNMoO}_2 \cdot 10\text{H}_2\text{O}$ .

This process is comparable to that just described for the preparation of the carbonato complex. In both cases the solution was completely reduced to molybdenum(III) by means of potassium iodide; in one case potassium cyanide is added and in the other carbon dioxide; both additions producing complexes.

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## AN OXALATO COMPLEX OF MOLYBDENUM $(\text{NH}_4)_4\text{Mo}(\text{OX})_4 \cdot 8\text{H}_2\text{O}^*$

By M. C. STEELE†

The oxalato trichelate salt  $\text{K}_3\text{Cr}(\text{C}_2\text{O}_4)_3$  is well known, but attempts to form a similar molybdenum compound have failed. Foerster and Fricke (1923) tried to produce an oxalate by dissolving  $\text{Mo}(\text{OH})_3$  in oxalic acid. Spittle and Wardlaw (1929), following the earlier methods of Chilesotti (1906), also tried to produce an oxalate with reduced molybdenum.

It seemed probable, however, that if the molybdenum was reduced electrolytically in the presence of the cation there would be a greater possibility of producing a complex of the type  $\text{R}_4\text{MoOX}_4$ . This procedure was found to be effective.

The complex is diamagnetic and like the octacyanides it is probable that the bond orbitals used in its formation are  $4d^4 5s^5 p^3$ .

### Experimental

*Ammonium Tetraoxalato Molybdenum(IV)*  $(\text{NH}_4)_4\text{Mo}(\text{OX})_4 \cdot 8\text{H}_2\text{O}$ .—Ammonium molybdate (10 g) and oxalic acid (20 g) were dissolved in water (250 ml). The solution was electrolysed using a sintered glass partition. The electrodes were a platinum anode and a mercury cathode ( $1\frac{1}{2}$  in. dia.). The electrolysis proceeded at 24 V, 2–3 A for 12–14 hr. The initial colour of the electrolyte was clear and slightly brown. At the beginning of electrolysis the colour became a golden-yellow changing to yellowish brown, and thence to a reddish brown when evolution of hydrogen set in at the cathode

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(the Mo(III) stage). The temperature rose to 75 °C during electrolysis and the final colour of the reduced electrolyte was red. The reduced electrolyte was removed from the cell without any protective atmosphere and was placed in the refrigerator for crystallization after filtration. (A small amount (1 to 2 g) of a brownish material of unknown composition separated. This was filtered off and washed with ethanol. Before washing with ethanol this precipitate began to change to a bluish colour on the surface as soon as the mother liquor had drained off.)

Ethanol was added to the filtrate and a yellowish brown precipitate formed. This precipitate was filtered off, washed with ethanol, and dried at 40 °C, yielding a light brown product (Found: Mo, 14.5; OX, 53.3; NH<sub>4</sub>, 10.8 per cent. Calc. for (NH<sub>4</sub>)<sub>4</sub>Mo(OX)<sub>4</sub>·8H<sub>2</sub>O: Mo, 14.5; OX, 53.6; NH<sub>4</sub>, 10.8 per cent).

The conductance for 10<sup>-3</sup>M is 730 mhos at 25 °C and this is comparable with the double salt (NH<sub>4</sub>)<sub>3</sub>MoCl<sub>6</sub>·NH<sub>4</sub>Cl·2H<sub>2</sub>O, 730 mhos (Steele 1955).

The oxalato complex charred at 60 °C. It is very soluble in water, giving a reddish brown solution, but is insoluble in common organic solvents.

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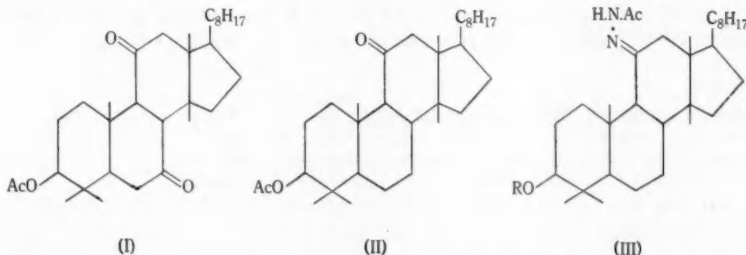
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# METHYLSTEROIDS\*†

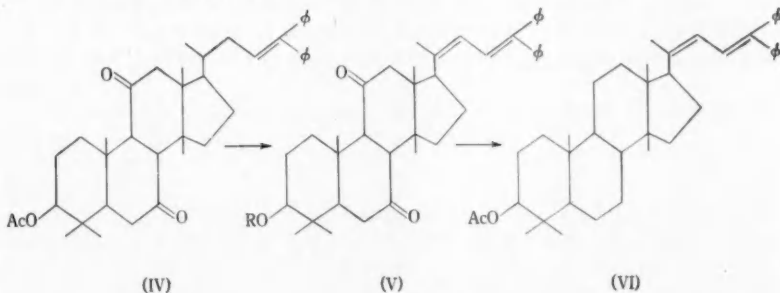
## IV. WOLFF-KISHNER REDUCTIONS OF DIKETONES DERIVED FROM LANOSTEROL

By C. S. BARNES‡

Wolff-Kishner reduction of the diketone I, under conditions designed to give the 7-deoxy compound II after acetylation, gave also a compound more strongly absorbed on alumina. By analogy with the works of Elks and Phillips (1956) and on the basis of the ultraviolet absorption spectrum and method of formation it is formulated as the acetylhydrazone of 3 $\beta$ -acetoxylanostan-11-one (III; R=Ac).



The phenylbutadiene (VI) has already been reported (Barnes 1956). It has now been prepared by a variation of the original route.



The diphenylethylene (IV) was converted with *N*-bromosuccinimide to give V (R=Ac) characterized also as the alcohol (V; R=H) and benzoate (V; R=Bz). Vigorous Wolff-Kishner reduction and acetylation of the product then gave VI.

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† Part III. Barnes and Palmer (1957).—*Aust. J. Chem.* **10**: 334.

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### Experimental

(a) *General*.—As in Part III (Barnes and Palmer 1957).

(b) *Wolff-Kishner Reduction of 7,11-Dioxolanostan-3 $\beta$ -yl Acetate (I)*.—Sodium (8 g) was treated with diethylene glycol (200 ml) and the diketone I (8 g) and hydrazine hydrate (20 ml; 90%) added. After heating to 180 °C for 18 hr, the product was isolated in the usual way and acetylated. Crystallization gave 11-oxolanostan-3 $\beta$ -yl acetate (II) (4 g). The remainder was chromatographed on alumina to give with benzene, more II. Benzene-ether mixtures eluted fractions which on crystallization gave 11-oxolanostan-3 $\beta$ -yl acetate 11-acetylhydrazone (III;  $R=Ac$ ) (1 g) which crystallized from chloroform-methanol to have m.p. 230–231 °C,  $[\alpha]_D +71^\circ$  (c, 1.3);  $\lambda_{max}$  217 m $\mu$ ,  $\epsilon$  14,000,  $\lambda_{inflex. c.}$  235 m $\mu$ ,  $\epsilon$  8000 (Found: C, 75.2; H, 10.7; N, 5.3%. Calc. for  $C_{34}H_{58}O_3N_2$ : C, 75.3; H, 10.7; N, 5.1%).

Hydrolysis with methanolic potassium hydroxide gave the derived alcohol (III;  $R=H$ ) crystallizing from methanol to have m.p. 218–220 °C,  $\lambda_{max}$  217 m $\mu$ ,  $\epsilon$  14,300;  $\lambda$  235,  $\epsilon$  9000 (Found: C, 76.2; H, 11.0; N, 5.8%. Calc. for  $C_{32}H_{56}O_3N_2$ : C, 76.7; H, 11.3; N, 5.6%).

(c) *7,11-Dioxo-24,24-diphenyl-25,26,27-trisnorlanosta-20(22),23-dien-3 $\beta$ -ol (V;  $R=H$ ) and Derivatives*.—The diphenylethylene (IV) (3 g) was oxidized in the usual way (Barnes 1956) with *N*-bromosuccinimide (1.2 g) in carbon tetrachloride solution (150 ml). Acetylation of the product gave 7,11-dioxo-24,24-diphenyl-25,26,27-trisnorlanosta-20(22), 23-dien-3 $\beta$ -yl acetate (V;  $R=Ac$ ) which crystallized from chloroform-methanol to have m.p. 237–240 °C,  $[\alpha]_D +26^\circ$  (c, 1.76);  $\lambda_{max}$  230 m $\mu$ ,  $\epsilon$  14,000;  $\lambda_{max}$  303 m $\mu$ ,  $\epsilon$  26,000 (Found: C, 81.0; H, 8.3; O, 10.7%. Calc. for  $C_{41}H_{50}O_4$ : C, 81.2; H, 8.3; O, 10.6%).

Hydrolysis by methanolic potassium hydroxide gave the derived alcohol (V;  $R=H$ ) which crystallized from chloroform-methanol to have m.p. 236–239 °C,  $[\alpha]_D +2^\circ$  (c, 1.4);  $\lambda_{max}$  305 m $\mu$ ,  $\epsilon$  30,000 (Found: C, 82.7; H, 8.4%. Calc. for  $C_{39}H_{48}O_3$ : C, 82.9; H, 8.5%).

Benzoylation of the alcohol with benzoyl chloride in pyridine for 1 hr (100 °C) gave the benzoate (V;  $R=Bz$ ) crystallizing from chloroform-methanol to have m.p. 262–264 °C,  $\lambda_{max}$  230 m $\mu$ ,  $\epsilon$  29,000;  $\lambda_{max}$  305 m $\mu$ ,  $\epsilon$  29,000 (Found: C, 82.7; H, 7.5%. Calc. for  $C_{48}H_{58}O_4$ : C, 82.6; H, 7.8%). The constants (m.p. 236–237 °C,  $[\alpha]_D +2^\circ$ ;  $\lambda_{max}$  310 m $\mu$ ,  $\log \epsilon$  4.52) recorded by McGhie *et al.* (1951) for this compound suggest they may have had the alcohol (V;  $R=H$ ).

(d) *Wolff-Kishner Reduction of 7,11-Dioxo-24,24-diphenyl-25,26,27-trisnorlanosta-20(22), 23-dien-3 $\beta$ -yl Acetate (V;  $R=Ac$ )*.—The dione (V;  $R=Ac$ ) (2.8 g) and anhydrous hydrazine (5 ml) were heated to 180 °C in diethylene glycol (100 ml) for 1 hr. A solution of the alkoxide made by reacting sodium (3 g) with diethylene glycol (100 ml) was added and heating continued for 18 hr. Working up in the usual way, acetylating, and crystallizing gave the 7,11-deoxy compound VI having m.p. 234–236 °C undepressed on mixing with that obtained previously (Barnes 1956). Chromic acid oxidation of VI gave the 20-ketone with identical m.p. and mixed m.p. with that obtained previously (Barnes 1956).

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